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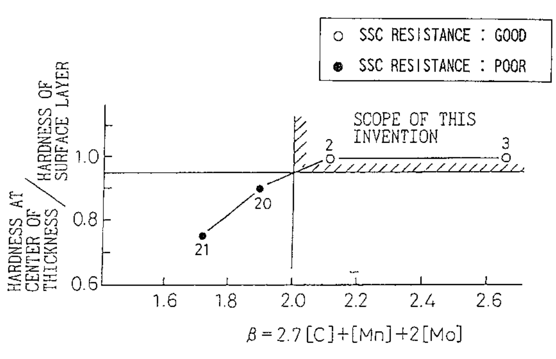
(54) STEEL PRODUCT FOR OIL WELL HAVING HIGH STRENGTH AND BEING EXCELLENT IN RESISTANCE TO SULFIDE STRESS CRACKING

(57) This invention provides a high-strength steel material for an oil well, excellent in strength and SSC resistance, and having a yield strength of at least 120 ksi. The steel material contains C: 0.10 to 0.40%, Si ≦ 0.5%, Mn ≦ 0.5%, P ≦ 0.015%, S ≦ 0.0050%, Mo: 0.5 to 2.5%, A1: 0.005 to 0.1%, Ti: 0.005 to 0.1% and at least 3.4 times N, Nb: 0.01 to 0.1%, N ≦ 0.01% and B: 0.0005 to 0.0050%, wherein the yield strength expressed by ksi and the Mo content satisfy the following relation (1), the balance of the C, Mn and Mo contents satisfies the following relation (2), and the steel material may contain, whenever necessary, at least one of Cr ≦ 0.2%, W ≦ 0.5%, V: 0.01 to 0.3%, Zr: 0.001 to 0.01%, Ca: 0.001 to 0.01%, Mg: 0.001 to 0.01% and REM: 0.001 to 0.01%.

$$\alpha = Mo - 0.15YS \geqq -18.9 \qquad (1)$$

$$\beta = 2.7C + Mn + 2Mo \geqq 2.0 \qquad (2)$$

Fig.1



(NUMERALS ON PLOTS REPRESENT NOS. OF EXAMPLES IN TABLE 2)

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Description

TECHNICAL FIELD:

[0001] This invention relates to a high-strength steel material such as a steel pipe, for example, casing, tubing, drill pipe, for an oil well, excellent in both strength and sulfide stress cracking (hereinafter referred to as "SSC") resistance, that is used in oil and gas wells while it is exposed to a sour gas environment.

BACKGROUND ART:

[0002] A steel material used for oil and gas wells containing hydrogen sulfide is required to possess SSC resistance. The true nature of this SSC is hydrogen embrittlement. Hydrogen embrittlement is more likely to occur as the strength of the steel material becomes higher. It has been therefore difficult to simultaneously satisfy the high strength and the high SSC resistance requirements.

[0003] With such a background, technical development has been done to obtain steel materials excellent in the SSC resistance and having high yield strength. For example, Japanese Examined Patent Publication (Kokoku) No.6-104849 describes a technology that achieves high strength, while SSC resistance is secured, by optimizing the steel components and the microstructure. However, the upper limit of the strength level that can be achieved by this technology presumably remains at a yield strength level of 120 ksi. Japanese Unexamined Patent Publication (Kokai) No.4-66645 discloses a technology that particularly addresses the interaction between Cr and Ni, and secures SSC performance and toughness with a higher strength by controlling the contents of these components. Nonetheless, the strength level that can be achieved by this technology is also, presumably, at the yield strength level of 120 ksi.

[0004] Market needs for oil well pipes have required, in recent years, a new type of steel material that has a yield strength of higher than about 125 ksi while it provides a sufficient SSC resistance. Demands for such a steel material are expected to grow in future.

[0005] Therefore, the yield strength of 120 ksi, that is, the level that has been achieved so for, is not sufficient to cope with the future needs, and development of a new type of steel is necessary.

DISCLOSURE OF THE INVENTION:

[0006] In view of the background described above, the present invention aims at providing a steel material having an excellent SSC resistance with a high strength of at least 120 ksi in terms of the yield strength, that has been difficult to achieve in the past.

[0007] The inventor of the present invention conducted a series of studies to solve the problems described above. As a result, the present inventor has acquired the knowledge necessary and sufficient to constitute the present invention.

[0008] When the strength of the steel material becomes high, SSC occurs from the grain boundary. To suppress such a rupture, the microstructure must first be uniform. To acquire a high strength of at least 120 ksi and a high SSC resistance, there is no other selection but to use tempered martensite as the microstructure, and this structure, must be as uniform as possible.

[0009] If any heterogeneous phase having different characteristics is contained in the microstructure, the boundary of this heterogeneous phase or the heterogeneous phase itself functions as a breaking start point, and a sufficient SSC resistance cannot be obtained. Uniformity of this structure is substantially determined by the condition of quenching. In other words whether or not the heterogeneous phase develops depends on whether or not a sufficient and uniform quenched martensite structure is obtained throughout the steel material. Needless to say, a complete full martensitic microstructure is preferred. In consideration of thick steel materials or the limitation of the contents of elements capable of contributing to hardenability, that will be described later, the present inventor has examined the condition that is essential to the high strength level to which the present invention is directed. Fig. 1 shows the result.

[0010] In Fig. 1, a 25 mm-thick sheet material is subjected to quenching with water cooling from the austenite temperature of 900 to 930°C. Next, the hardness at the center portion of the thickness, that is, the most distant from the quenched end of the steel material, and the hardness of the portion just below the material surface that is just below the quenched end are measured. Hardenability is evaluated in terms of the ratio of the hardness of the former to that of the latter. At the same chance, a test specimen is machined from the center portion of the thickness to evaluate the SSC resistance.

[0011] The present inventor has acquired from Fig. 1 the knowledge that, when the ratio of the hardness of the center portion of the thickness to the hardness just below the plate surface is at least 95%, sufficient SSC resistance can be obtained even at a high strength of 120 ksi or more. The present inventor has also acquired the knowledge that, in order to sufficiently harden a steel material having a thickness of about 25 mm, an index β (2.7C + Mn + 2Mo) calculated from the C, Mn and Mo contents must be at least 2.0.

[0012] The present inventor has examined the relationship between the strength that governs SSC performance, and the contents of the alloy elements, on the premise of the uniform microstructure without the heterogeneous phase, and has discovered the results shown in Fig. 2, wherein the relationship between Mo content and yield strength YS of the steel material after tempering is plotted. The contents of Mn and P affecting SSC performance was controlled to the lowest level that can be accomplished industrially. The relationship can be shown extremely clearly. The present inventor has found that to secure sufficient SSC resistance in a high strength material of YS ≧ 120 ksi, the Mo content must be at least 0.5%, and the α value expressed by the relation with the yield strength YS, that is, α = Mo (wt%) - 0.15YS (ksi), must be at least -18.9.

[0013] However, there is the case where the target cannot be achieved even after the uniform microstructure described above is obtained and, moreover, even after the effect of the effective element Mo is exploited. As a result of the analysis of this case, the present inventor has found that even a slight difference in the Cr content exerts great influence on the high strength material as the object of the present invention.

[0014] The present inventor has examined the relationship between YS and the Cr content under the condition that the microstructure after the quenching is kept uniform, the content of SSC resistance deteriorating elements such as P and Mn are also kept at a sufficiently low level and constant, and moreover, the useful Mo content is kept constant. As a result, the present inventor has found that the SSC resistance varies greatly in the Cr content range of 0.2 to 0.25% as shown in Fig. 3. In Fig. 3, the SSC threshold stress can be improved by about 10 ksi by limiting the Cr content to not greater than 0.28.

[0015] Chromium (Cr) has been utilized positively in the past as the element necessary for securing hardenability. However, it should be understood that Cr is an element that is detrimental to SSC in a high strength region exceeding 120 ksi, because Cr rather weakens the grain boundary strength as the carbide precipitating element and affects SSC harmfully. Therefore Cr content should be restricted.

[0016] Furthermore, the present inventor has examined in detail the influences of Mn and Mo after P is set to a low level and Cr is restricted. As a result, the present inventor has found that both components interact as shown in Fig. 4. In the region where the Mn content is 0.3% or below, the SSC resistance depends solely on the Mo content. Within the range of the Mn content of 0.3 to 0.5%, however, the Mo content must be increased so as to correspond to the increase of the Mn content. When the Mn content exceeds 0.5%, the SSC resistance cannot be improved and further even when the Mo content is increased. Therefore, in order to make the most of the utility of Mo, the Mn content must be limited to 0.5% or below, and preferably to less than 0.3%.

[0017] The present invention has been completed on the basis of the observations described above. The gist of the present invention resides in the following points.

(1) A high-strength steel material for an oil well, excellent in sulfide stress cracking resistance, containing, in terms of mass%:

C: 0.10 to 0.40%, Si ≦ 0.5%,
Mn ≦ 0.5%, P ≦ 0.015%,
S ≦ 0.0050%, Mo: 0.5 to 2.5%,
Al: 0.005 to 0.1%,
Ti: 0.005 to 0.1% and at least 3.4 times N%,
Nb: 0.01 to 0.1%, N ≦ 0.01% and
B: 0.0005 to 0.0050%,

wherein the yield strength YS expressed by ksi and the Mo content satisfy the following relation (1) and the balance of the C, Mn and Mo contents satisfies the following relation (2).

$$\alpha = \text{Mo} - 0.15\text{YS} \geqq -18.9 \quad (1)$$

$$\beta = 2.7\text{C} + \text{Mn} + 2\text{Mo} \geqq 2.0 \quad (2)$$

(2) A high-strength steel material for an oil, excellent in sulfide stress cracking resistance, containing, in terms of mass%:

C: 0.10 to 0.40%, Si ≦ 0.5%,
Mn ≦ 0.5%, P ≦ 0.015%,

S ≦ 0.0050%, Mo: 0.5 to 2.5%,
Al: 0.005 to 0.1%,
Ti: 0.005 to 0.1% and at least 3.4 times N%,
Nb: 0.01 to 0.1%, N ≦ 0.01% and
B: 0.0005 to 0.0050%,

wherein the yield strength YS expressed by ksi and the Mo content satisfy the following relation (1) and the balance of C, Mn and Mo contents satisfies the following relation (2); and
wherein the steel material contains further at least one of the following elements:

Cr ≦ 0.2%, W ≦ 0.5%
V: 0.01 to 0.3%, Zr: 0.001 to 0.010%,
Ca: 0.001 to 0.01%, Mg: 0.001 to 0.01% and
REM: 0.001 to 0.01%.

$$\alpha = Mo - 0.15YS \geqq -18.9 \quad (1)$$

$$\beta = 2.7C + Mn + 2Mo \geqq 2.0 \quad (2)$$

(3) A high-strength steel material for an oil well, excellent in sulfide stress cracking resistance, containing, in terms of mass%:

C: 0.10 to 0.40%, Si ≦ 0.5%,
Mn < 0.3 %, P ≦ 0.015%,
S ≦ 0.0050%, Mo: 0.5 to 2.5%,
Al: 0.005 to 0.1%,
Ti: 0.005 to 0.1% and at least 3.4 times N%,
Nb: 0.01 to 0.1%, N ≦ 0.01% and
B: 0.0005 to 0.0050%,

wherein the yield strength YS expressed by ksi and the Mo content satisfy the following relation (1) and the balance of the C, Mn and Mo contents satisfies the following relation (2).

$$\alpha = Mo - 0.15YS \geqq -18.9 \quad (1)$$

$$\beta = 2.7C + Mn + 2Mo \geqq 2.0 \quad (2)$$

(4) A high-strength steel material for an oil well, excellent in sulfide stress cracking resistance, containing, in terms of mass%:

C: 0.10 to 0.40%, Si ≦ 0.5%,
Mn< 0.3%, P ≦ 0.015%,
S ≦ 0.0050%, Mo: 0.5 to 2.5%,
Al: 0.005 to 0.1%,
Ti: 0.005 to 0.1% and at least 3.4 times N%,
Nb: 0.01 to 0.1%, N ≦ 0.01% and
B: 0.0005 to 0.0050%,

wherein the yield strength YS expressed by ksi and the Mo content satisfy the following relation (1) and the balance of the C, Mn and Mo contents satisfies the following relation (2); and
wherein said steel material further contains at least-one of the following elements:

Cr ≦ 0.2%, W ≦ 0.5%,
V: 0.01 to 0.3%, Zr: 0.001 to 0.010%,

Ca: 0.001 to 0.01%, Mg: 0.001 to 0.01% and
REM: 0.001 to 0.01%.

$$\alpha = Mo - 0.15YS \geqq -18.9 \quad (1)$$

$$\beta = 2.7C + Mn + 2Mo \geqq 2.0 \quad (2)$$

(5) A high-strength steel material for an oil well, excellent in sulfide stress cracking resistance and having a yield strength of at least 120 ksi, containing, in terms of mass%:

C: 0.10 to 0.40%, Si ≦ 0.5%,
Mn< 0.5%, P ≦ 0.015%,
S ≦ 0.0050%, Mo: 0.5 to 2.5%,
Al: 0.005 to 0.1%,
Ti: 0.005 to 0.1% and at least 3.4 times N%,
Nb: 0.01 to 0.1%, N ≦ 0.01% and
B: 0.0005 to 0.0050%,

wherein the yield strength YS expressed by ksi and the Mo content satisfy the following relation (1) and the balance of the C, Mn and Mo contents satisfies the following relation (2).

$$\alpha = Mo - 0.15YS \geqq -18.9 \quad (1)$$

$$\beta = 2.7C + Mn + 2Mo \geqq 2.0 \quad (2)$$

(6) A high-strength steel material for an oil well, excellent in sulfide stress cracking resistance and having a yield strength of at least 120 ksi, containing, in terms of mass%:

C: 0.10 to 0.40%, Si ≦ 0.5%,
Mn < 0.5%, P ≦ 0.015%,
S ≦ 0.0050%, Mo: 0.5 to 2.5%,
Al: 0.005 to 0.1%,
Ti: 0.005 to 0.1% and at least 3.4 times N%,
Nb: 0.01 to 0.1%, N ≦ 0.01% and
B: 0.0005 to 0.0050%,

wherein the yield strength YS expressed by ksi and the Mo content satisfy the following relation (1) and the balance of the C, Mn and Mo contents satisfies the following relation (2); and

wherein said steel material further contains at least one of the following elements:

Cr ≦ 0.2%, W ≦ 0.5%,
V: 0.01 to 0.3%, Zr: 0.001 to 0.010%,
Ca: 0.001 to 0.01%, Mg: 0.001 to 0.01% and
REM: 0.001 to 0.01%.

$$\alpha = Mo - 0.15YS \geqq -18.9 \quad (1)$$

$$\beta = 2.7C + Mn + 2Mo \geqq 2.0 \quad (2)$$

(7) A high-strength steel material for an oil well, excellent in sulfide stress cracking resistance and having a yield strength of at least 120 ksi, containing, in terms of mass%:

C: 0.10 to 0.40%, Si ≦ 0.5%,

Mn< 0.3%, P ≦ 0.015%,
S ≦ 0.0050%, Mo: 1.0 to 2.5%,
Al: 0.0050 to 0.1%,
Ti: 0.005 to 0.1% and at least 3.4 times N%,
Nb: 0.01 to 0.1%, N ≦ 0.01% and
B: 0.0005 to 0.0050%,

wherein the yield strength YS expressed by ksi and the Mo content satisfy the following relation (1) and the balance of the C, Mn and Mo contents satisfies the following relation (2).

$$\alpha = Mo - 0.15YS \geqq -18.9 \quad (1)$$

$$\beta = 2.7C + Mn + 2Mo \geqq 2.0 \quad (2)$$

(8) A high-strength steel material for an oil well, excellent in sulfide stress cracking resistance and having a yield strength of at least 120 ksi, containing, in terms of mass%:

C: 0.10 to 0.40%, Si ≦ 0.5%,
Mn < 0.3%, P ≦ 0.015%,
S ≦ 0.0050%, Mo: 1.0 to 2.5%,
Al: 0.005 to 0.1%,
Ti: 0.0050 to 0.1% and at least 3.4 times N%,
Nb: 0.01 to 0.1%, N ≦ 0.01% and
B: 0.0005 to 0.0050%,

wherein the yield strength YS expressed by ksi and the Mo content satisfy the following relation (1) and the balance of the C, Mn and Mo contents satisfies the following relation (2); and

wherein said steel material further contains at least one of the following elements:

Cr ≦ 0.2%, W ≦ 0.5%,
V: 0.01 to 0.3%, Zr: 0.001 to 0.010%,
Ca: 0.001 to 0.01%, Mg: 0.001 to 0.01% and
REM: 0.001 to 0.01%.

$$\alpha = Mo - 0.15YS \geqq -18.9 \quad (1)$$

$$\beta = 2.7C + Mn + 2Mo \geqq 2.0 \quad (2)$$

(9) A method of producing a high-strength steel material for an oil well, excellent in sulfide stress cracking resistance, said method comprising the steps of hot processing the steel containing the components according to any of (1) through (8) and having the balance of the C, Mn and Mo contents satisfying the following relation (2);

heating for austenitizing the steel material to a temperature within the range of [Ac_3 point + 20°C] to 1,000°C;

quenching the steel material to obtain a microstructure in which the hardness as-quenched at the remotest position in the steel from the cooled surface thereof is at least 95% of the hardness of the cooled surface; and

tempering the steel material at a temperature of 620 to 720°C.

$$\beta = 2.7C + Mn + 2Mo \geqq 2.0 \quad (2)$$

(10) A high-strength steel material for an oil well, excellent in sulfide stress cracking, according to any of (1) through (9),

wherein a threshold stress for crack occurrence determined by a constant load type sulfide stress cracking test according to NACE TM0177-A is at least 80% of the yield strength.

BRIEF DESCRIPTION OF THE DRAWINGS:

[0018]

Fig. 1 is a graph showing a ratio of the hardness at the center portion of the thickness in the as-quenched state to the hardness of the portion immediately below the surface layer, by a hardenability index β, and showing also the relationship between the SSC resistance of the steel material after quenching and β.

Fig. 2 is a graph showing the SSC resistance of a steel having high hardenability by the relationship between the Mo content and YS.

Fig. 3 is a graph showing the SSC resistance of a steel having high hardenability and a constant Mo content in terms of the relationship between YS and a Cr content.

Fig. 4 is a graph showing the SSC resistance of a steel having an equivalent YS in association with the Mn and Mo contents.

Fig. 5 is a graph showing the SSC resistance in terms of the ratio of a threshold stress for crack ocurrence to YS as an index of the SSC resistance when YS changes.

BEST MODE FOR CARRYING OUT THE INVENTION:

[0019] Hereinafter, the present invention will be explained in detail.

[0020] First, the reasons for limitation of the alloy components in the present invention will be explained. The content of each component is expressed in percent by weight.

[0021] C: Carbon is an essential element for securing simultaneously the intended high strength and the SSC resistance. The strength and the SSC resistance depend on hardenability. When the C content is less than 0.10%, quenching becomes incomplete and the strength drops. Even if required strength can be secured by adjusting the tempering condition, a sufficient SSC resistance cannot be acquired. When the C content exceeds 0.40%, on the other hand, the SSC resistance gets into saturation and susceptibility to quench crack and delayed fracture increases. Therefore, an appropriate range of the C content is set to the range of 0.10 to 0.40%.

[0022] Si: Silicon exists as a residue of a deoxidizer used in the steel making process. When the Si content exceeds 0.5%, the steel becomes brittle and the SSC resistance deteriorates. Therefore, the upper limit is set to 0.5%.

[0023] Mn: Manganese is an element detrimental to the SSC resistance and should not be added. However, since Mn has the function of improving hardenability, up to 0.5% as the upper limit of Mn may be contained in case that the C and Mo contents for improving hardenability are small and hardenability is not sufficient. When Mn is contained in the amount exceeding 0.5%, a satisfactory SSC resistance cannot be obtained even when complete quenching is conducted. Therefore the upper limit is set to 0.5%. Incidentally the preferred content of Mn is less than 0.3%.

[0024] P: Phosphorus is an impurity element which deteriorates the SSC resistance as it segregates in the grain boundary. Therefore, the P content must be restricted to as low as possible. The upper limit of the P content is set to 0.015% as an allowable level that can be attained stably according to existing refining technologies in view of the cost.

[0025] S: Sulfur is also an element that segregates in the grain boundary and deteriorates the SSC resistance. It is a basic requirement in the present invention to inhibit the Mn content that fixes S. Therefore, the S content should be reduced as low as possible. Since remarkable deterioration of the SSC resistance is not observed at a S content of less than 0.0050%, the upper limit is set to 0.0050%.

[0026] Mo: Molybdenum is one of the essential elements in the present invention. It is the element that restricts the grain boundary segregation of P and improves the temper softening resistance. Therefore, Mo is a suitable element for obtaining the high strength. At least 0.5% of Mo must be contained in order to secure a sufficient SSC resistance in the high strength region of YS $\geqq$ 120 ksi as shown in Fig. 2. The higher YS, the greater the Mo amount that is to be contained. The preferred range is at least 1.0%. When Mo is contained in a greater amount, the effect gets into saturation, and freedom of strength adjustment becomes small. Therefore, the upper limit is set to 2.5%.

[0027] Al: Aluminum is necessary for sufficiently deoxidizing the steel during the steel making process, and at least 0.005% of Al should be contained. When a greater amount of Al is contained, however, the amounts of alumina type inclusions increase with the result that the susceptibility to SSC is likely to increase. Therefore, the upper limit is set to 0.1%.

[0028] Ti: Titanium is contained in order to let B, that will be described later, sufficiently exhibit its hardenability enhancing function. In other words, N must be fixed as TiN in advance in order to prevent precipitation of BN. For this purpose, at least 0.005%, and moreover, at least 3.4 times the N content, of Ti must be added. However, a greater Ti content promotes precipitation of TiN and enhances SSC susceptibility. Therefore, the upper limit is set to 0.1%.

[0029] Nb: Niobium is the element effective for improving the SSC resistance because it reduces the grain boundary segregation of P through its grain refining effect. Therefore, at least 0.01% of Nb is contained. However, even when a greater amount of Nb is contained, the grain refining effect gets into saturation. On the contrary, the SSC resistance drops due to the drop of the grain boundary strength resulting from coarsening of carbides. Hence, the upper limit is set to 0.1%.

[0030] N: Nitrogen is an impurity element that hinders the hardenability improving effect of B and should be restricted to as low as possible. The upper limit is set to 0.01% as the allowable level that can be attained industrially and stably by the existing refining technologies in view of the cost.

[0031] B: Boron is the element that remarkably improves hardenability, and is one of the essential elements in the present invention for securing hardenability. If the B content is less than 0.0005%, sufficient hardenability cannot be secured. Therefore, the lower limit is set to 0.0005%. If the B content exceeds 0.0050%, on the other hand, the hardenability improving effect gets into saturation, and precipitation of carbo-borides becomes remarkable and the SSC resistance gets deteriorated, on the contrary. Therefore, the upper limit is set to 0.0050%.

$$\alpha = \text{Mo} - 0.15\text{YS}:$$

[0032] When the value α, that is calculated as the function of the yield strength YS (ksi) and the Mo content (wt%), exceeds -18.9 as shown in Fig. 2, an excellent SSC resistance can be obtained. When it is below -18.9, a satisfactory SSC resistance cannot be obtained even when the individual components satisfy the respective conditions. For this reason, the present invention stipulates a $\geqq$ -18.9 as the essential requirement of the invention in addition to the component conditions described above.

$$\beta = 2.7\text{C} + \text{Mn} + 2\text{Mo}:$$

[0033] In addition to the component conditions described above, the index β, that is calculated from the contents (wt%) of the alloy elements contributing to hardenability, such as C, Mn and Mo, is set to at least 2.0, as shown in Fig. 1, in order to secure sufficient hardenability. The upper limit is calculated as 6.11 from each of the upper limit contents of C, Mn and Mo.

[0034] In addition to the elements described above, the steel material of the present invention may contain at least one element selected from the following elements, whenever necessary.

[0035] Cr: Chromium is a useful element for improving hardenability, but need not be contained if sufficient hardenability can be secured by other elements such as Mo. In the steel material having a yield strength of 120 ksi or more, the Cr content exceeding 0.2% deteriorates the SSC resistance. Therefore, its upper limit is set to 0.2%.

[0036] W: Tungsten has the function of improving both hardenability and temper softening resistance. However, its effect is not sufficient if its content is less than 0.01%. When the content exceeds 0.5%, the effect gets into saturation. Therefore the suitable range of the W content is set to 0.01 to 0.5%.

[0037] V: Vanadium has the function of improving temper softening resistance. When its content is greater than 0.01%, it is effective for improving the strength. When an excessive amount of V is contained, however, the SSC resistance gets deteriorated. Therefore, the upper limit is set to 0.3%.

[0038] Zr: Zirconium has an effect of restricting grain boundary segregation of P. At least 0.001% of Zr must be contained in order to obtain the effect. Zr is an expensive element and, if contained too much, Zr increases the amounts of oxides and possibly increases the SSC susceptibility. Therefore, the upper limit is set to 0.010%.

[0039] Ca, Mg and REM: These elements mitigate the stress concentration by spheroidizing the morphology of inclusions, at the same time, mitigate the grain boundary segregation of S by fixing it. If the content of these elements is less than 0.001%, the effect is small. On the other hand, at an excessive content, the amounts of oxides increase and the SSC susceptibility is possibly enhanced. Therefore, the upper limit of these element is set to 0.010%.

[0040] In the present invention, the steel having the alloy composition described above is molten in a converter or an electric furnace and cast. It is then shaped by an ordinary hot rolling method into a desired shape such as a pipe, a sheet or rod, is subjected to quenching and tempering, and is refined to a desired strength.

[0041] The heat-treating condition in the present invention will be explained as follows.

[0042] The austenitizing temperature for quenching is at least [Ac_3 point + 20°C] and not higher than 1,000°C. If it is lower than Ac_3 point + 20°C, austenitizing of the steel material is not sufficient and a uniform martensite structure cannot be obtained easily. When the austenitizing temperature exceeds 1,000°C, on the other hand, the grain growth becomes remarkable and the area of the grain boundary decreases . In consequence, the SSC resistance deteriorating effect of the segregation elements such as P becomes remarkable. Therefore, the suitable austenitizing temperature is within the range of [Ac_3 + 20°C] to 1,000°C. Incidentally, the typical Ac_3 point of the steel material according to the present invention is 830°C.

[0043] As described above, further, the steel material quenched from this austenitizing temperature must have a uniform structure in order to acquire a satisfactory SSC resistance. It is necessary that the hardness of the portion that is most distant from the quenched end has a value of at least 95% in terms of the ratio to the hardness of the portion immediately below the quenched end. In the chemical composition of the present invention, expected hardenability can be secured even in a thick material having a thickness of about 25 mm.

[0044] A suitable range of the tempering temperature is 620 to 720°C. Under the low temperature condition of lower than 620°C, YS becomes excessively high and the value α described above becomes low. In consequence, the satisfactory SSC resistance cannot be obtained. When the tempering temperature exceeds 720°C, on the other hand, the temperature is in the dual phase region, and uniformity of the microstructure is lost with the result of an increase of the SSC susceptibility. Therefore, the range of 630 to 720°C is set as the suitable condition for a tempering temperature.

[0045] The YS value can be secured within the predetermined range due to the heat treatment temperature range described above, for example, by controlling the quenching temperature, and the relation α = Mo - 0.15YS ≧ -18.9 can be satisfied.

[0046] As described above, it is possible to obtain a high strength, SSC-resistant steel material satisfying YS 120 ksi, which has not been achieved in the past, by optimizing the microstructure and the components. When the present invention is applied to the strength region of YS of lower than 120 ksi, the SSC resistance ca also be improved. Fig. 5 shows the measurement result of the threshold stress for crack occurrence (σth) of a steel material, that satisfies the microstructure and the chemical compositions of the present invention and is refined to YS of 117 to 120 ksi, while the applied stress is varied by a NACE TM0177-A constant load SSC test. It can be thus said that the structural factors of the present invention improve not only the SSC resistance of the steel material having YS ≧ 120 ksi but also that of the steel material having YS of less than 120 ksi due to the improvement of σth.

EXAMPLE:

[0047] Each steel material having a chemical composition tabulated in Table 1 was molten in a vacuum melting furnace, and the resulting ingot was hot rolled to a plate having a thickness of 25 mm. The plate was heated to 900 to 1,025°C for austenitizing, and was then subjected to quenching treatment by water. The hardness at the center of the thickness and the hardness of a portion just below the surface were measured. Hardenability was evaluated by calculating their ratio. Subsequently, tempering was conducted at 630 to 730°C. A round rod tensile test specimen was machined from the center of the thickness of this plate, and the tensile test was carried out.

[0048] A test specimen for a sulfide stress cracking test, which had a round rod shape having a length of 25 mm at parallel portions and a diameter of 6.2 mm and was stipulated in NACE-TM0177-A, was also machined from the center of the thickness. This test was carried out in a corrosive solution containing 0.5% acetic acid + 5% NaCl and containing H_2S saturated at a partial pressure of 1 atm at 25°C, for 720 hours while a constant stress corresponding to 80% of the yield strength was loaded to the specimen. Additional tests were carried out by decreasing the applied stress step-wise by 5%YS, whenever necessary, for those specimens which underwent rupture at the applied stress of 80%YS, and by increasing the applied stress step-wise by 5%YS for those specimens which did not undergo rupture. In this way, a threshold stress for crack occurrence (σth) was determined.

[0049] Hardenability was evaluated as "good" when the hardness of the center portion of the thickness was greater than 95% of the hardness of the portion immediately below the surface. The SSC resistance was evaluated as "good" for those specimens which did not undergo rupture during the test for 720 hours. The test result was tabulated in Tables 2 and 3.

[0050] Nos. 1 to 11 and Nos. 101 to 104 represent the test results that fell within the range of the present invention. These specimens satisfied both high strength of YS 120 ksi and excellent SSC resistance.

[0051] On the other hand, Nos. 18 to 30 and Nos. 105 to 107 of Comparative Examples could not provide excellent SSC resistance because their components were outside the range of the present invention. The components of Nos. 12, 13, 14, 16 and 17 of Comparative Examples were within the range of the present invention but the α values were outside the range of the present invention. Nos. 15 and 31 of Comparative Examples could not provide sufficient SSC resistance because the tempering temperature and the austenitizing temperature were outside the range of the present invention, respectively.

[0052] In Nos. 108 and 109 tabulated in Table 3, YS was less than 120 ksi but σth was higher than that of Comparative Examples Nos. 113 and 114 having an equivalent YS value. Therefore, the SSC resistance was improved. Nos. 110 and 111 had the YS values higher than 120 ksi and their σth values, were as high as 85% of YS. On the other hand, in Comparative Example No. 112, YS remained at 85% of σ th though YS was low. No. 115 had insufficient SSC resistance.

Table 1 Chemical Compositions (wt %; * ppm)

Item	Symbol	C	Si	Mn	P*	S*	Mo	Al	Ti	Nb	N*	B*	Ti/N	Cr	W	V	Zr*	Ca*	Mg*	REM*	β
This Invention	X-1	0.20	0.15	0.06	80	15	1.30	0.025	0.021	0.026	39	12	5.38								3.20
	X-2	0.20	0.16	0.46	81	15	1.30	0.026	0.022	0.031	41	13	5.37								3.60
	X-3	0.27	0.15	0.15	70	25	0.58	0.029	0.031	0.019	55	13	5.64								2.04
	X-4	0.29	0.15	0.04	60	10	1.51	0.025	0.026	0.026	39	12	6.67			0.21					3.84
	A	0.29	0.15	0.45	81	10	0.90	0.040	0.035	0.029	70	15	5.00	0.14	0.25	0.02		21			3.03
	B	0.20	0.15	0.33	70	25	0.62	0.029	0.031	0.019	55	13	5.64								2.11
	C	0.20	0.15	0.33	70	15	0.89	0.029	0.031	0.019	55	13	5.64	0.19							2.65
	D	0.20	0.20	0.13	81	25	1.40	0.036	0.075	0.021	39	7	19.23								3.47
	E	0.19	0.25	0.08	86	16	1.80	0.038	0.021	0.031	41	38	5.12				15			15	4.19
	F	0.12	0.15	0.23	57	9	2.21	0.047	0.029	0.041	51	11	5.69								4.97
	G	0.19	0.20	0.05	75	10	1.50	0.035	0.041	0.031	45	21	9.11	0.10				21	12		3.56
Comparative Example	Y-1	0.23	0.16	0.30	80	16	0.78	0.024	0.023	0.025	44	11	5.23	0.40							2.48
	Y-2	0.25	0.15	0.13	80	16	0.42	0.025	0.025	0.025	38	12	6.58								1.65
	Y-3	0.21	0.16	0.55	80	16	1.88	0.026	0.024	0.029	41	12	5.85								4.88
	H	0.15	0.21	0.30	91	25	1.55	0.026	0.008	0.018	65	13	1.90					19			3.81
	I	0.28	0.15	0.46	135	21	0.48	0.032	0.040	0.036	39	20	10.30	0.15							2.18
	J	0.17	0.14	0.21	70	23	0.61	0.036	0.025	0.038	46	13	5.43								1.89
	K	0.12	0.15	0.20	75	28	0.60	0.046	0.036	0.030	55	12	6.55								1.72
	L	0.25	0.16	0.33	51	18	1.40	0.040	0.034	0.034	51	56	6.67								3.81
	M	0.19	0.17	0.45	165	14	0.75	0.032	0.033	0.036	55	15	6.00								2.46
	N	0.25	0.15	0.33	71	16	0.91	0.031	0.031	0.039	56	13	5.54	0.34							2.83
	O	0.18	0.15	0.60	136	13	0.71	0.033	0.035	0.029	60	12	5.83								2.51
	P	0.19	0.14	0.36	129	55	0.72	0.026	0.029	0.034	78	9	3.71								2.31
	Q	0.23	0.15	0.33	71	16	0.91	0.031	0.031	0.039	56	13	5.54	0.25							2.77
	R	0.21	0.18	0.31	120	20	1.19	0.034	0.021	0.111	40	13	5.25								3.26

The underlined values are out of the scope of the invention.

Table 2 Heat Treatment Conditions, Strength and SSC Test Results

Item	No.	Composition	Quenching Temperature (°C)	Hardenability	Tempering Temperature (°C)	YS (ksi)	α	SSC Test Results under conditions of load stress = 80% of YS
This Invention	101	X-1	950	Good	670	126	-17.90	Good
	102	X-2	930	Good	670	125	-17.45	Good
	103	X-3	930	Good	670	123	-17.87	Good
	104	X-4	930	Good	710	131	-18.14	Good
	1	A	900	Good	680	123	-17.85	Good
	2	B	900	Good	670	124	-17.98	Good
	3	C	900	Good	660	125	-17.86	Good
	4	C	930	Good	650	129	-18.46	Good
	5	D	900	Good	670	129	-17.95	Good
	6	E	900	Good	700	131	-17.85	Good
	7	E	930	Good	680	136	-18.60	Good
	8	E	900	Good	720	121	-16.35	Good
	9	F	900	Good	690	135	-18.04	Good
	10	F	930	Good	680	138	-18.49	Good
	11	G	930	Good	670	131	-18.15	Good
Comparative Example	105	Y-1	930	Good	650	124	-17.82	Poor
	106	Y-2	930	Poor	650	123	-18.03	Poor
	107	Y-3	930	Good	690	124	-16.72	Poor
	12	C	900	Good	640	134	-19.21	Poor
	13	C	900	Good	630	140	-20.11	Poor
	14	E	900	Good	680	141	-19.35	Poor
	15	E	900	Good	730	103	-15.27	Poor
	16	G	930	Good	660	145	-20.25	Poor
	17	G	900	Good	660	137	-19.05	Poor
	18	H	900	Poor	650	129	-17.80	Poor
	19	I	930	Good	690	125	-18.27	Poor
	20	J	900	Poor	650	119	-17.24	Poor
	21	K	900	Poor	650	115	-16.65	Poor
	22	L	930	Good	700	131	-18.25	Poor
	23	M	900	Good	660	128	-18.45	Poor
	24	N	900	Good	650	129	-18.44	Poor
	25	N	900	Good	670	118	-16.79	Good
	26	O	930	Good	660	126	-18.19	Poor
	27	P	900	Good	660	128	-18.19	Poor
	28	Q	900	Good	650	125	-17.84	Poor
	29	Q	900	Good	660	118	-16.79	Good
	30	R	900	Good	670	130	-18.31	Poor
	31	C	1025	Good	660	130	-18.61	Poor

The underlined data are out of the scope of the invention.

Table 3 Heat Treatment Conditions, Strength and SSC Test Results

Item	No.	Composition	Quenching Temperature (℃)	Hardenability	Tempering Temperature (℃)	YS (ksi)	α	σth (×YS)
This Invention	108	X-1	950	Good	690	111	-15.35	0.95
	109	X-1	950	Good	680	119	-16.55	0.90
	110	X-1	950	Good	670	126	-17.90	0.85
	111	X-1	950	Good	660	132	-18.50	0.85
Comparative Example	112	<u>Y-1</u>	950	Good	690	106	-15.12	0.85
	113	<u>Y-1</u>	950	Good	680	112	-16.02	0.85
	114	<u>Y-1</u>	950	Good	670	118	-16.92	0.80
	115	<u>Y-1</u>	950	Good	660	121	-18.42	0.55

The underlined data are out of the scope of the invention.

INDUSTRIAL APPLICABILITY

[0053] According to the present invention, as described above, a steel material for an oil well that satisfies both a high strength of at least 120 ksi in terms of a yield strength and excellent SSC resistance can be produced.

Claims

1. A high-strength steel material, for an oil well, excellent in sulfide stress cracking resistance, containing, in terms of mass%:

C: 0.10 to 0.40%, Si ≦ 0.5%,
Mn ≦ 0.5%, P ≦ 0.015%,
S ≦ 0.0050%, Mo: 0.5 to 2.5%,
Al: 0.005 to 0.1%,
Ti: 0.005 to 0.1% and at least 3.4 times N%,
Nb: 0.01 to 0.1%, N ≦ 0.01% and
B: 0.0005 to 0.0050%,

wherein the yield strength YS expressed by ksi and the Mo content satisfy the following relation (1) and the balance of the C, Mn and Mo contents satisfies the following relation (2).

$$\alpha = Mo - 0.15YS \geqq -18.9 \quad (1)$$

$$\beta = 2.7C + Mn + 2Mo \geqq 2.0 \quad (2)$$

2. A high-strength steel material, for an oil, excellent in sulfide stress cracking resistance, containing, in terms of mass%:

C: 0.10 to 0.40%, Si ≦ 0.5%,
Mn ≦ 0.5%, P ≦ 0.015%,
S ≦ 0.0050%, Mo: 0.5 to 2.5%,
Al: 0.005 to 0.1%,
Ti: 0.005 to 0.1% and at least 3.4 times N%,
Nb: 0.01 to 0.1%, N < 0.01% and
B: 0.0005 to 0.0050%,

wherein the yield strength YS expressed by ksi and the Mo content satisfy the following relation (1) and the balance of C, Mn and Mo contents satisfies the following relation (2);

$$\alpha = Mo - 0.15YS > -18.9 \quad (1)$$

$$\beta = 2.7C + Mn + 2Mo \geqq 2.0 \quad (2),$$

and
wherein said steel material contains further at least one of the following elements:

Cr ≦ 0.2%, W ≦ 0.5%
V: 0.01 to 0.3%, Zr: 0.001 to 0.010%,
Ca: 0.001 to 0.01%, Mg: 0.001 to 0.01% and
REM: 0.001 to 0.01%.

3. A high-strength steel material, for an oil well, excellent in sulfide stress cracking resistance, containing, in terms of mass%:

C: 0.10 to 0.40%, Si ≦ 0.5%,
Mn < 0.3%, P ≦ 0.015%,
S ≦ 0.0050%, Mo: 0.5 to 2.5%,
Al: 0.005 to 0.1%,
Ti: 0.005 to 0.1% and at least 3.4 times N%,
Nb: 0.01 to 0.1%, N ≦ 0.01% and
B: 0.0005 to 0.0050%,

wherein the yield strength YS expressed by ksi and the Mo content satisfy the following relation (1) and the balance of the C, Mn and Mo contents satisfies the following relation (2).

$$\alpha = Mo - 0.15YS \geqq -18.9 \quad (1)$$

$$\beta = 2.7C + Mn + 2Mo \geqq 2.0 \quad (2)$$

4. A high-strength steel material, for an oil well, excellent in sulfide stress cracking resistance, containing, in terms of mass%:

C: 0.10 to 0.40%, Si ≦ 0.5%,
Mn< 0.3%, P ≦ 0.015%,
S≦ 0.0050%, Mo: 0.5 to 2.5%,
Al: 0.005 to 0.1%,
Ti: 0.005 to 0.1% and at least 3.4 times N%,
Nb: 0.01 to 0.1%, N ≦ 0.01% and
B: 0.0005 to 0.0050%,

wherein the yield strength YS expressed by ksi and the Mo content satisfy the following relation (1) and the balance of the C, Mn and Mo contents satisfies the following relation (2); and

Wherein said steel material contains further at least one of the following elements:

Cr ≦ 0.2%, W ≦ 0.5%,
V: 0.01 to 0.3%, Zr: 0.001 to 0.010%,
Ca: 0.001 to 0.01%, Mg: 0.001 to 0.01% and
REM: 0.001 to 0.01%.

$$\alpha = Mo - 0.15YS \geqq -18.9 \quad (1)$$

$$\beta = 2.7C + Mn + 2Mo \geqq 2.0 \quad (2)$$

5. A high-strength steel material, for an oil well, excellent in sulfide stress cracking resistance and having a yield strength of at least 120 ksi, containing, in terms of mass%:

C: 0.10 to 0.40%, Si ≦ 0.5%,
Mn < 0.5%, P ≦ 0.015%,
S ≦ 0.0050%, Mo: 0.5 to 2.5%,
Al: 0.005 to 0.1%,
Ti: 0.005 to 0.1% and at least 3.4 times N%,
Nb: 0.01 to 0.1%, N ≦ 0.01% and
B: 0.0005 to 0.0050%,

wherein the yield strength YS expressed by ksi and the Mo content satisfy the following relation (1) and the balance of the C, Mn and Mo contents satisfies the following relation (2).

$$\alpha = Mo - 0.15YS \geqq -18.9 \quad (1)$$

$$\beta = 2.7C + Mn + 2Mo \geqq 2.0 \quad (2)$$

6. A high-strength steel material, for an oil well, excellent in sulfide stress cracking resistance and having a yield strength of at least 120 ksi, containing, in terms of mass%:

C: 0.10 to 0.40%, Si ≦ 0.5%,
Mn ≦ 0.5%, P ≦ 0.015%,
S ≦ 0.0050%, Mo: 0.5 to 2.5%,
Al: 0.005 to 0.1%,
Ti: 0.005 to 0.1% and at least 3.4 times N%,
Nb: 0.01 to 0.1%, N ≦ 0.01% and
B: 0.0005 to 0.0050%,

wherein the yield strength YS expressed by ksi and the Mo content satisfy the following relation (1) and the balance of the C, Mn and Mo contents satisfies the following relation (2); and

wherein said steel material further contains at least one of the following elements:

Cr ≦ 0.2%, W ≦ 0.5%,
V: 0.01 to 0.3%, Zr: 0.001 to 0.010%,
Ca: 0.001 to 0.01%, Mg: 0.001 to 0.01% and
REM: 0.001 to 0.01%.

$$\alpha = Mo - 0.15YS \geqq -18.9 \quad (1)$$

$$\beta = 2.7C + Mn + 2Mo \geqq 2.0 \quad (2)$$

7. A high-strength steel material for an oil well, excellent in sulfide stress cracking resistance and having a yield strength of at least 120 ksi, containing, in terms of mass%:

C: 0.10 to 0.40%, Si ≦ 0.5%,
Mn < 0.3%, P ≦ 0.015%,
S ≦ 0.0050%, Mo: 1.0 to 2.5%,
Al: 0.0050 to 0.1%,
Ti: 0.005 to 0.1% and at least 3.4 times N%,
Nb: 0.01 to 0.1%, N ≦ 0.01% and
B: 0.0005 to 0.0050%,

wherein the yield strength YS expressed by ksi and the Mo content satisfy the following relation (1) and the balance of the C, Mn and Mo contents satisfies the following relation (2).

$$\alpha = Mo - 0.15YS \geqq -18.9$$

$$\beta = 2.7C + Mn + 2Mo \geqq 2.0 \qquad (2)$$

8. A high-strength steel material for an oil well, excellent in sulfide stress cracking resistance and having a yield strength of at least 120 ksi, containing, in terms of mass%:

C: 0.10 to 0.40%, Si ≦ 0.5%,
Mn < 0.3%, P ≦ 0.015%,
S ≦ 0.0050%, Mo: 1.0 to 2.5%,
Al: 0.005 to 0.1%,
Ti: 0.0050 to 0.1% and at least 3.4 times N%,
Nb: 0.01 to 0.1%, N ≦ 0.01% and
B: 0.0005 to 0.0050%,

wherein the yield strength YS expressed by ksi and the Mo content satisfy the following relation (1) and the balance of the C, Mn and Mo contents satisfies the following relation (2); and
wherein said steel material further contains at least one of the following elements:

Cr ≦ 0.2%, W ≦ 0.5%,
V: 0.01 to 0.3%, Zr: 0.001 to 0.010%,
Ca: 0.001 to 0.01%, Mg: 0.001 to 0.01% and
REM: 0.001 to 0.01%.

$$\alpha = Mo - 0.15YS \geqq -18.9 \qquad (1)$$

$$\beta = 2.7C + Mn + 2Mo \geqq 2.0 \qquad (2)$$

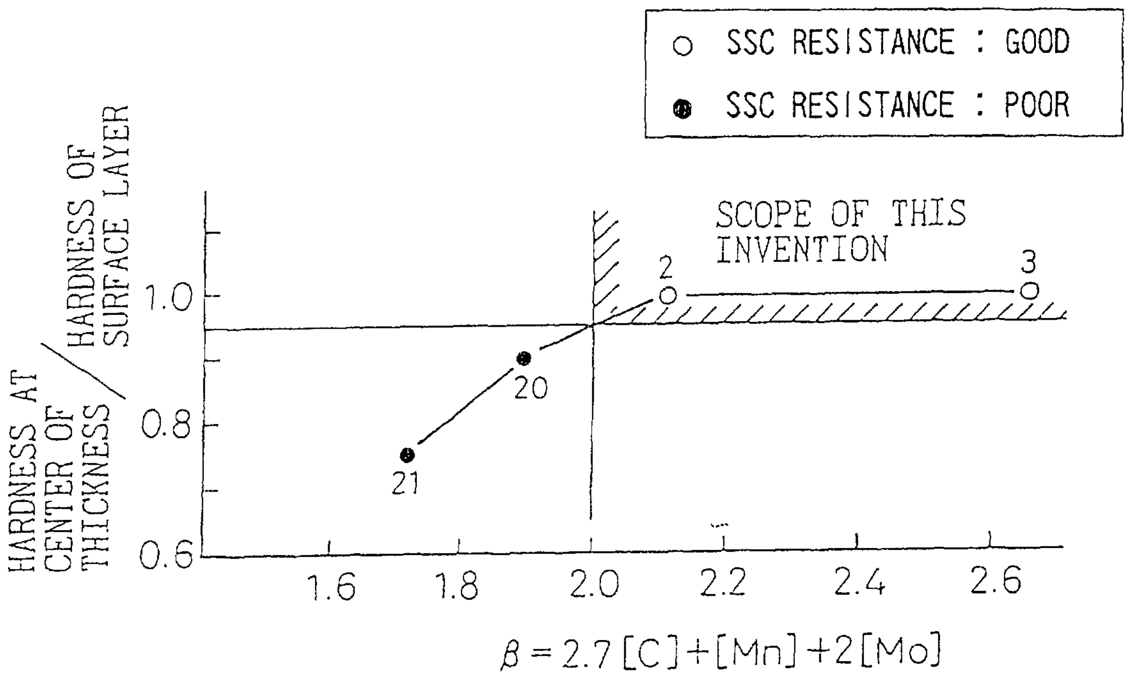
9. A method of producing a high-strength steel material, for an oil well, excellent in sulfide stress cracking resistance, said method comprising the steps of:

hot processing said steel containing said components according to any of claims 1 through 8 and having the balance of the C, Mn and Mo contents satisfying the following relation (2); heating for austenitizing said steel material to a temperature within the range of [Ac_3 point + 20°C] to 1,000°C;
quenching said steel material to obtain a microstructure in which the hardness as-quenched at the remotest position of said steel material from the cooled surface thereof is at least 95% of the hardness of the cooled surface; and
tempering said steel material at a temperature of 620 to 720°C.

$$\beta = 2.7C + Mn + 2Mo \geqq 2.0 \quad (2)$$

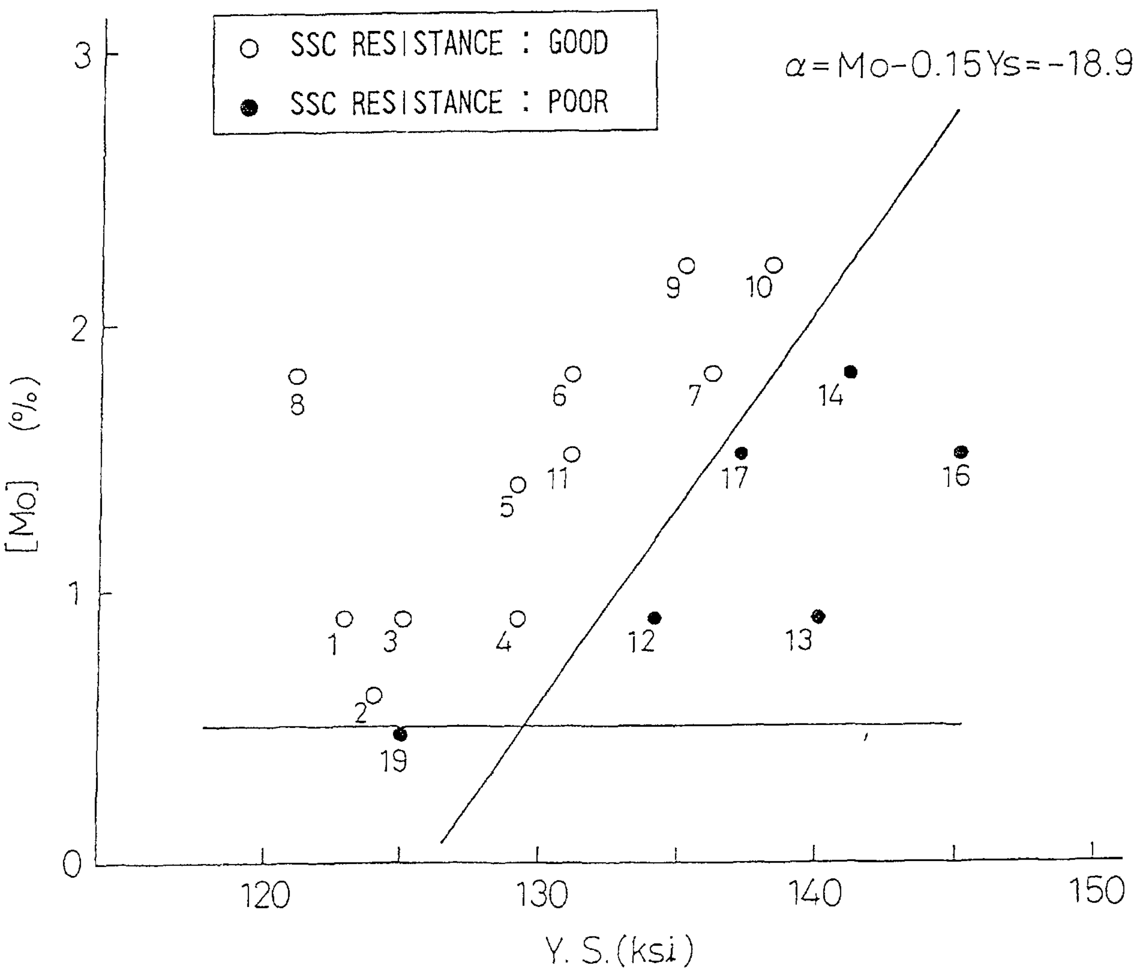
10. A high-strength steel material for an oil well excellent in sulfide stress cracking, according to any of claims 1 through 9, wherein a threshold stress for crack occurrence determined by a constant load type sulfide stress cracking test according to NACE TM0177-A is at least 80% of the yield strength.

Fig.1



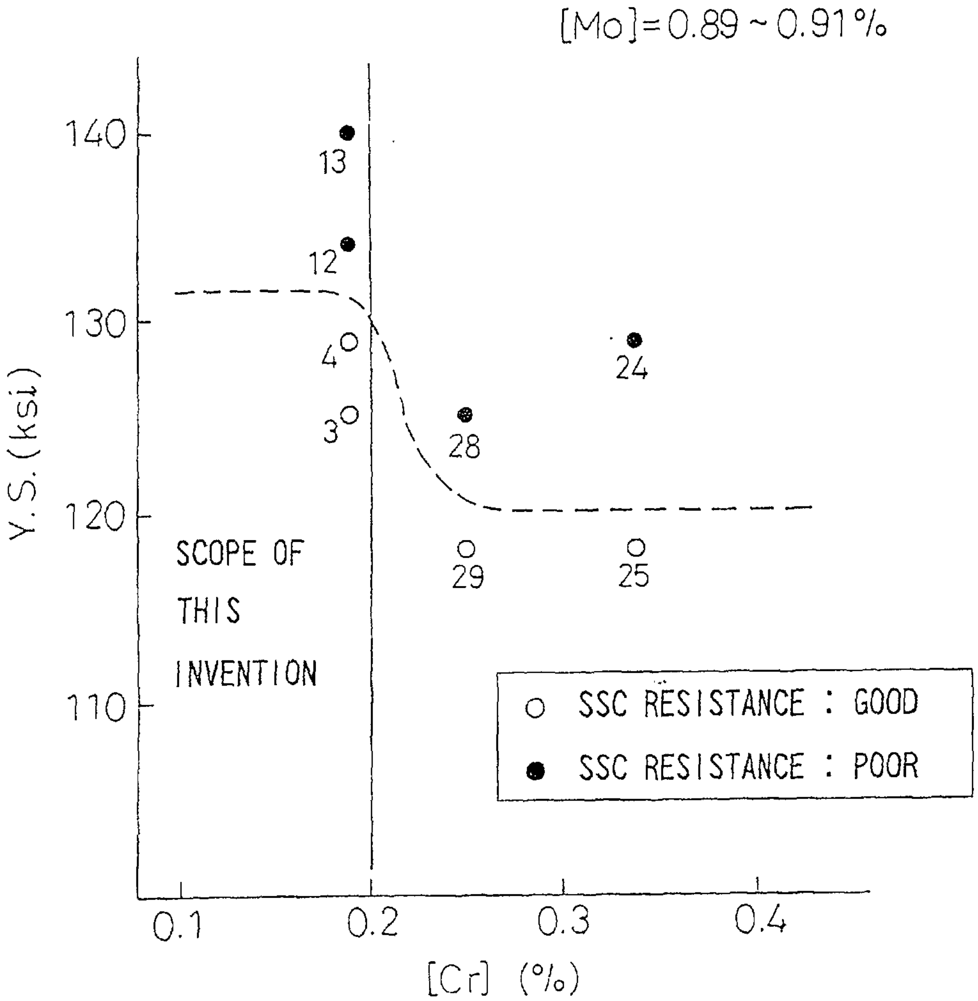
(NUMERALS ON PLOTS REPRESENT NOS. OF EXAMPLES IN TABLE 2)

Fig. 2



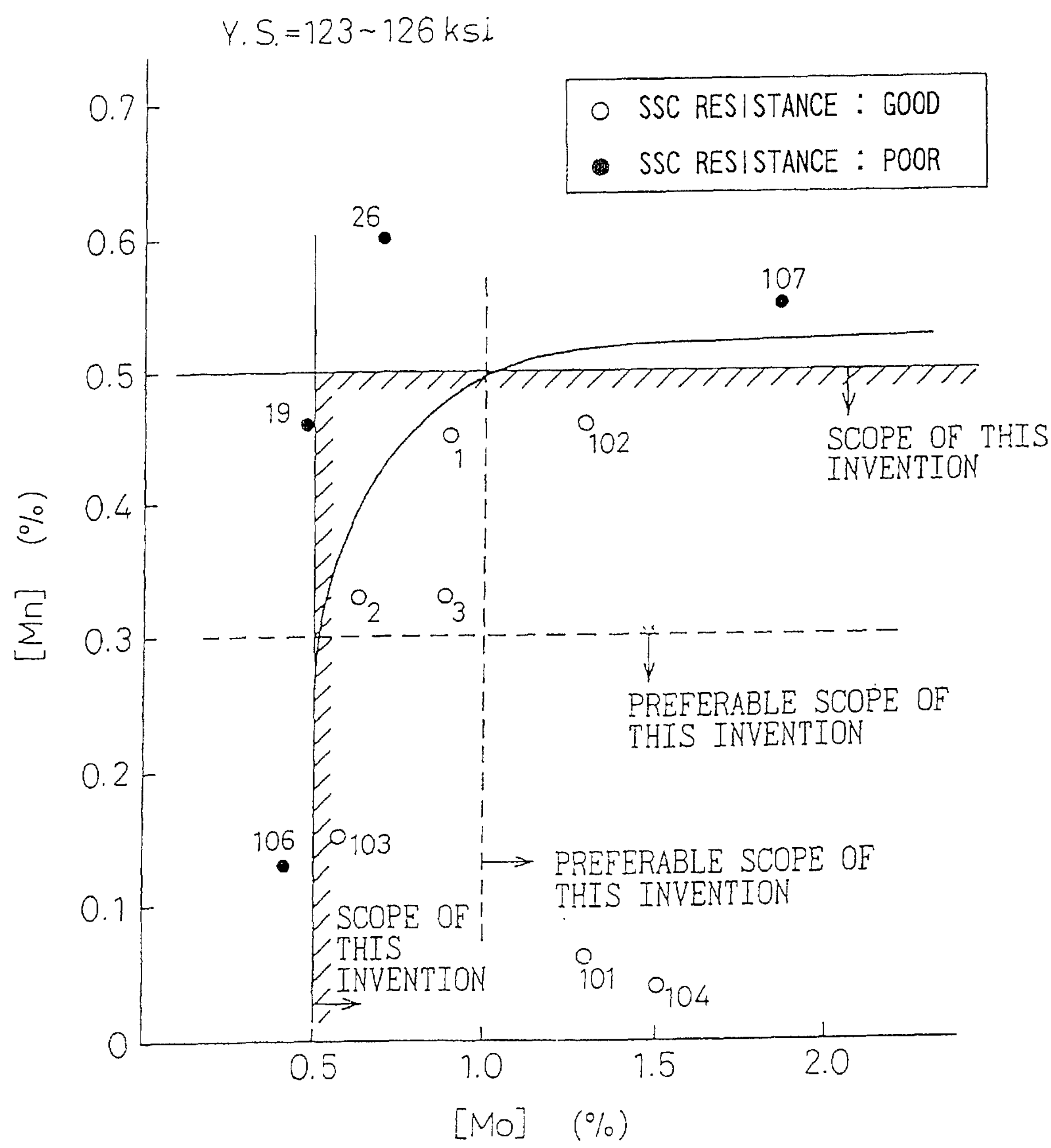
(NUMERALS ON PLOTS REPRESENT NOS. OF EXAMPLES IN TABLE 2)

Fig. 3



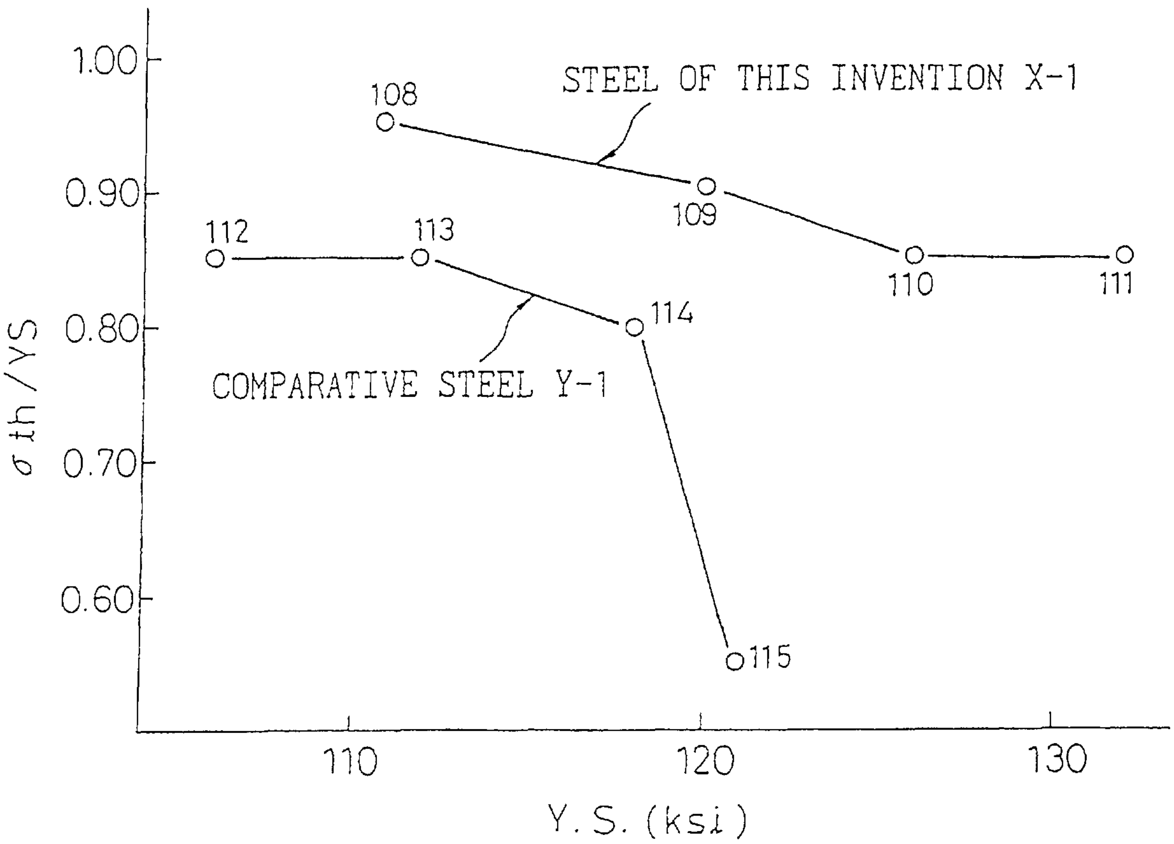
(NUMERALS ON PLOTS REPRESENT NOS. OF EXAMPLES IN TABLE 2.)

Fig. 4



(NUMERALS ON PLOTS REPRESENT NOS. OF EXAMPLES)

Fig. 5



(NUMERALS ON PLOTS REPRESENT NOS. OF EXAMPLES)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP00/02917

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl^7 C22C 38/00, 38/14, 38/32, C21D6/00

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)
Int.Cl^7 C22C 38/00, 38/14, 38/32, C21D6/00

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

Jitsuyo Shinan Koho	1926-1996	Toroku Jitsuyo Shinan Koho	1994-2000
Kokai Jitsuyo Shinan Koho	1971-2000	Jitsuyo Shinan Toroku Koho	1996-2000

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP, 6-104849, B (Nippon Steel Corporation), 21 December, 1994 (21.12.94), Claims (Family: none)	1,3,9,10
X	JP, 5-271772, A (Nippon Steel Corporation), 19 October, 1993 (19.10.93), Claims (Family: none)	1~4,9,10
X	JP, 9-67624, A (Sumitomo Metal Industries, Ltd.), 11 March, 1997 (11.03.97), implementation example (Family: none)	1,3,9,10
X	JP, 6-116635, A (Kawasaki Steel Corporation), 26 April, 1994 (26.04.94), implementation example (Family: none)	1,5,9,10
PX	JP, 11-335731, A (Sumitomo Metal Industries, Ltd.), 07 December, 1999 (07.12.99), Claims (Family: none)	2,4,6 8~10
A	JP, 63-4043, A (Sumitomo Metal Industries, Ltd.), 09 January, 1988 (09.01.88) (Family: none)	1~10

☐ 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 August, 2000 (01.08.00)	Date of mailing of the international search report 08 August, 2000 (08.08.00)
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
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