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(54) **process for producing extra high tensile steel having excellent stress corrosion cracking resistance**

Verfahren zum Herstellen von hochfestem Stahl mit ausgezeichneter Beständigkeit gegen Spannungsrisskorrosion

Procédé pour la production d'acier à très haute résistance présentant une excellente résistance à la fissuration par corrosion sous contrainte

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US-A- 4 946 516

- **PATENT ABSTRACTS OF JAPAN vol. 16, no. 63 (C-911)18 February 1992 & JP-A-03 260 012 (NIPPON STEEL CORPORATION) 20 November 1991**

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Description

[0001] The present invention relates to a process for producing an extra-high-tensile and high-toughness steel having a yield strength of 1080 MPa or more that has a high strength despite a low carbon content and is excellent in stress corrosion resistance in a stress corrosive environment, such as sea water and salt water.

[0002] In recent years, geophysical exploration on an earth scale, such as search and drilling for energy resources and occurrence of earthquake, has led to a growing interest in ocean development in deep sea and activated the construction and installation of various containers for deep-sea use and the development of research ships for deep-sea use.

[0003] When various containers are used in a deep-sea environment, since a very high pressure is applied thereto, it is required for materials for these containers to have a high degree of toughness and strength from the viewpoint of structure.

[0004] In order to cope with the demand for safe, reliable, high-strength and high-toughness materials, the development of a Ni-containing low alloy steel and an improvement in the quality thereof have been effected in the art. For example, proposals have been made on many production processes, such as a process for producing a high-strength and high-toughness steel comprising Ni-Cr-Mo-V with $C + 1/8Mo + V > 0.26$ and $Cr \leq 0.8$ Mo as disclosed in Japanese Unexamined Patent Publication (Kokai) No. 56-9358, a process for producing a Ni-Cr-Mo-V-based extra high tensile steel as disclosed in Japanese Unexamined Patent Publication (Kokai) No. 57-188655, which enables a high strength and a high toughness to be provided in a wide cooling rate range in a quenching treatment, and a process for a Ni-containing steel product, wherein very low P and very low S treatments are effected for the purpose of ensuring a high toughness. Although these processes are effective for increasing strength or toughness, there is a possibility that the reliability of the steel products produced by the above processes is poor in the environment contemplated in the present invention. Specifically, since the containers used in deep sea are exposed to sea water, the steel products should have a satisfactory resistance to corrosion in sea water, that is, a high resistance to stress corrosion cracking in sea water.

[0005] Examples of extra high tensile steel products having a high reliability underwater include a Ni-Cr-Mo-V-based high-toughness and extra-high-tensile steel proposed in Japanese Examined Patent Publication (Kokoku) No. 64-11105, characterized by comprising a Ni-containing steel having lowered N and O contents and capable of satisfying a requirement of Al (%) x N (%) x $10^4 < 1.5$, which high-toughness and extra-high-tensile steel has a significant effect. In this steel, however, the stress corrosion cracking resistance at the welding heat affected zone in sea water is inferior to that in the air as compared with the base material, which requires further study regarding improvement in safety and reliability. On the other hand, Japanese Examined Patent Publication (Kokoku) No. 1-51526 proposes a process for producing an extra high tensile steel having an excellent stress corrosion cracking resistance, which comprises subjecting a Ni-Mo-Nb-based steel having a Ni content of 5 to 8% to direct quenching-and-tempering. The strength of the steel product, however, is lower than that contemplated in the present invention. In the production of a thick high tensile steel by the direct quenching-and-tempering process, close control is necessary from the viewpoint of the homogeneity and anisotropy of the quality in the direction of the plate thickness. Further, there is a possibility that the stability of the quality is deteriorated in the widthwise direction and longitudinal direction within the steel plate.

[0006] Thus, the conventional extra high tensile steel products have lower stress corrosion cracking resistance particularly at the welding-heat affected zone in sea water than in the air and are produced by processes that are disadvantageous in the homogeneity of the quality in the thicknesswise direction of the thick steel plate and the stability of the quality within the steel plate. That is, a further improvement in both the steel products and production processes has been desired in the art.

[0007] A steel which meets the compositional requirements of the present invention is disclosed in US-A-4 814 141 (Table 1, Steel N), specific parameters of hot working and heat treating after hot working being not mentioned therein. Such parameters, similar to those claimed, are disclosed in US-A-4 946 516, however without any specific rate of reheating being disclosed.

[0008] An object of the present invention is to improve the homogeneity of the quality of a thick steel product through an alleviation in the problem of the prior art, i.e., a problem of the stress corrosion cracking resistance, particularly a deterioration in the stress corrosion cracking resistance at the welding heat affected zone in sea water, together with an increase in the tensile strength. The subject matter of the present invention is as follows.

[0009] A process for producing an extra high tensile steel having an excellent stress corrosion cracking resistance, comprises the steps of: heating a slab comprising, in terms of % by weight, 0.04 to 0.09% of C, 0.01 to 0.10% of Si, 0.05 to 0.65% of Mn, 8.0 to 11.0% of Ni, 0.5 to 1.5% of Mo, 0.2 to 1.5% of Cr, 0.02 to 0.20% of V and 0.01 to 0.08% of Al with the balance consisting of iron and unavoidable impurities or a slab comprising the above-described ingredients and further comprising at least one member selected from the group consisting of 0.2 to 1.5% of Cu, 0.005 to 0.10% of Nb and 0.005 to 0.03% of Ti as strength improving elements and 0.0005 to 0.005% of Ca and 0.0005 to 0.0100% of REM (Rare earth metal) as elements having a capability of regulating the form of inclusions to a temperature between 1000°C and 1250°C, hot-rolling the slab at a temperature of Ar' point (the term "Ar' point" being used because, in the

steel of the present invention, ferrite is not formed from the austenitic state even at the Ar3 transformation point and there occurs $\gamma \rightarrow \gamma'$) or above, air-cooling the rolled plate, reheating the rolled plate at a rate of 120°C/min or less to a temperature region of from (A_{c3} point - 40°C) to (A_{c3} point + 40°C), quenching the reheated plate and subsequently tempering the quenched plate at a temperature of the A_{c1} point or below.

Fig. 1 is a diagram showing the relationship between the Mn content and the stress corrosion cracking resistance of a steel product;

Fig. 2 is a diagram showing the relationship between the temperature rise rate during reheating and the yield strength;

Fig. 3 is a schematic view of a metallic microstructure in connection with a reheating temperature region, wherein (A) is a metallic microstructure for a reheating temperature region of (A_{c3} point - 40°C) or below, (B) is a metallic microstructure for a reheating temperature region falling within the scope of the present invention and (C) is a metallic microstructure for a reheating temperature region of (A_{c3} point + 40°C) or above;

Fig. 4 is a diagram showing the relationship between the yield strength and the K_{ISCC} value of the base material of an example of the present invention; and

Fig. 5 is a diagram showing a notch position for the evaluation of K_{ISCC} value in the welding-heat affected zone in an example of the present invention;

[0010] The present inventors have conducted various studies on steel ingredients and production process, particularly on hot rolling, reheating, quenching and tempering with a view to stably producing a Ni-containing low alloy steel having a good resistance to stress corrosion cracking, particularly stress corrosion cracking at the welding-heat affected zone, in sea water or salt water and, at the same time, a high tensile strength and a high toughness and, as a result, have found that, when Mo, V and Nb are added to a Ni-containing steel having lowered C, Si and Mn contents and the Ni-containing steel is hot-rolled to sufficiently dissolve these elements in a solid solution form and reheated and quenched with controlled temperature rise rate and heating temperature range, the Mo, V and Nb dissolved in a solid solution form are precipitated during heating to form non-diffusion type reverse transformed γ grains comprising a group of acicular austenites having a high dislocation density, which enables a reinforcing mechanism inherent in the Ni-containing steel to be exhibited to attain an increase in the strength.

[0011] At the outset, the reason for the limitation of ingredients of the steel according to the present invention will now be described.

[0012] C is an element useful for improving the quenchability and easily increasing the strength. On the other hand, it has the greatest effect on an improvement in the stress corrosion cracking resistance of the welding-heat affected zone of the extra high tensile steel. When the content exceeds 0.09%, a significant lowering in the stress corrosion cracking resistance of the welding-heat affected zone occurs. On the other hand, when it is lower than 0.04%, the strength is unsatisfactory. For this reason, the C content is limited to 0.04 to 0.09%.

[0013] Si is useful for improving the strength. It is also indispensable for steel making. Si is contained in an amount of 0.01% at the smallest. In the case of a high Ni-containing steel contemplated in the present invention, when the Si content exceeds 0.10%, the temper brittleness becomes so great that the low-temperature toughness is lowered. For this reason, the Si content is limited to 0.01 to 0.10%.

[0014] Mn is necessary for improving the quenchability and hot workability. However, when the Mn content is less than 0.05%, the improvement effect cannot be attained. On the other hand, in the case of the Ni-containing steel contemplated in the present invention, the addition of Mn increases the susceptibility to temper brittleness and deteriorates the stress corrosion cracking resistance of the welding-heat affected zone, so that the Mn content should be 0.65% or less. Fig. 1 shows the toughness and the results of a stress corrosion cracking test (K_{ISCC} test) in artificial sea water for steel plates produced by subjecting a slab having a composition of 0.06% C - 9.9% Ni - 1.0% Mo - 0.1% V with the amount of addition of Mn being varied from 0.15 to 1.05% to hot rolling and air cooling, reheating the cooled plate to 770°C, quenching the reheated plate and tempering the quenched plate at 540°C. It is apparent that the low-temperature toughness and the stress corrosion cracking resistance are improved with lowering the Mn content. For this reason, the Mn content is limited to 0.05 to 0.65%.

[0015] Ni is useful for enhancing the stacking fault energy, increasing the cross slip, facilitating the occurrence of stress relaxation, increasing the impact absorption energy and improving the low-temperature toughness.

[0016] Further, Ni exhibits the best effect when it is present together with Mo, V and other elements contained in the steel of the present invention. Specifically, when the steel is reheated to a temperature region of from (A_{c3} point - 40°C) to (A_{c3} point + 40°C), a grain mixture of diffusion type reverse transformed γ grains comprising a massive austenite formed by dissolution of carbides with non-diffusion type reverse transformed γ grains comprising a group of acicular austenites not involving the dissolution of carbides is formed, and the non-diffusion type reverse transformed γ grains have a higher dislocation density than the diffusion type reverse transformed γ grains and very effectively contributes to an increase in the strength. Specifically, Ni serves to delay the dissolution of carbides of Mo, V and other elements,

which enables the group of acicular austenites to be stably maintained up to a high temperature. For this reason, Ni should be added in an amount of 8.0% or more for the purpose of ensuring the strength by taking advantage of stabilization of the non-diffusion type reverse transformed γ grains at a high temperature. On the other hand, when the amount of addition of Ni exceeds 11.0%, austenite is precipitated during tempering, which deteriorates the strength and toughness. For this reason, the Ni content is limited to 8.0 to 11.0%.

[0017] Mo is an element useful for the precipitation hardening by tempering and the inhibition of temper brittleness and, at the same time, important to the present invention as with Ni. Specifically, since a fine carbide composed mainly of Mo precipitated in the course of heating in the step of reheating and quenching remains as an undissolved carbide up to a high temperature, the group of acicular austenites having a high dislocation density can be maintained at a high temperature, so that Mo is necessary for ensuring the strength. However, when the Mo content is less than 0.5%, the dissolution of the Mo carbide occurs in the reheating and quenching, which causes the non-diffusion type transformed γ grains to be rapidly attacked by the diffusion type reverse transformed γ grains, so that a contemplated strength cannot be obtained. On the other hand, when the Mo content exceeds 1.5%, the effect of improving the strength is saturated, so that the amount of coarse alloy carbides is increased to lower the toughness. For this reason, the Mo content is limited to 0.5 to 1.5%.

[0018] Cr serves to improve the quenchability and is useful for ensuring the strength. The Cr content should be 0.2% at the lowest. When it exceeds 1.5%, the increase in the strength is saturated and the toughness is lowered. For this reason, the Cr content is limited to 0.2 to 1.5%.

[0019] V is useful for forming a carbonitride in the tempering that is precipitation-hardened to ensure the strength. Further, as with Mo, V is finely precipitated during heating in the reheating and quenching to increase the stability of non-diffusion type reverse transformed γ grains comprising a group of acicular austenites, which is useful for ensuring the strength. When the V content is less than 0.02%, no contemplated strength cannot be attained, while when it exceeds 0.20%, the toughness is lowered. For this reason, the V content is limited to 0.02 to 0.20%.

[0020] Al is necessary for deoxidation and, at the same time, combines with N to form a nitride, AlN, that has the effect of refining the structure. However, when the Al content is less than 0.01%, this effect is small. On the other hand, when it exceeds 0.08%, the amount of inclusions comprising alumina becomes so large that the toughness is inhibited. For this reason, the Al content is limited to 0.01 to 0.08%.

[0021] In one embodiment of the present invention, at least one member selected from (Cu, Nb, Ti) and (Ca, REM) is added besides the above-described ingredients. Cu, Nb and Ti exhibit an equalizing action, that is, serve to improve the strength of the steel. Further, Nb and Ti are useful also for the refinement of austenite grains. In order to ensure a desired effect, it is necessary for the lower limits of Cu, Nb and Ti to be 0.2%, 0.005% and 0.005%, respectively. However, when the Cu, Nb and Ti contents exceed 1.5%, 0.10% and 0.03%, respectively, not only the low-temperature toughness is lowered but also the susceptibility to stress corrosion cracking is enhanced. For this reason, the Cu, Nb and Ti contents are limited to the above-described respective ranges.

[0022] Ca and REM (Rare earth metal) have the effect of spheroidizing nonmetallic inclusions and are useful for improving both the toughness and anisotropy. For this purpose, the Ca and REM should be present in an amount of 0.0005% at the smallest. However, when the Ca and REM contents exceed 0.005% and 0.0100%, respectively, the toughness is lowered due to an increase in the amount of inclusions. For this reason, the Ca and REM contents are limited to 0.0005 to 0.005% and 0.0005 to 0.0100%, respectively.

[0023] The steel of the present invention contains, besides the above-described ingredients, P, S, N, O and other elements as unavoidable impurities that are detrimental to the toughness and stress corrosion cracking resistance characteristic of the steel of the present invention and, therefore, the amount of these unavoidable impurities is as small as possible. The contents of P, S, N and O are preferably regulated to 0.005% or less, 0.003% or less, 0.0050% and 0.0030%, respectively.

[0024] The production process which is another subject matter of the present invention will now be described.

[0025] Even when the steel comprises the above-described composition, the production process should be proper for attaining the strength, toughness and stress corrosion cracking resistance contemplated in the present invention. Accordingly, in the process of the present invention, the rolling, cooling and reheating-quenching-tempering conditions were limited for the following reasons.

[0026] At the outset, a slab comprising the above-described ingredients is heated to 1000 to 1250°C. In the heating, in order to attain, besides the refinement of heated austenite grains, utilization of the strengthening by taking advantage of the above-described non-diffusion type reverse transformed γ and fine precipitation in the reheating-quenching-tempering after the hot rolling, the slab should be heated to 1000°C or above to sufficiently dissolve Mo, Cr, V, Nb, etc., in a solid solution form. In this case, when the temperature is below 1000°C, the dissolution of these elements in a solid solution form is unsatisfactory and the alloy carbide (M_6C) remaining undissolved is coarsened, which makes it impossible to expect sufficient precipitation hardening in the tempering and, at the same time, is causative of a lowering in the toughness. On the other hand, when the temperature exceeds 1250°C, although alloy carbides of Mo, Cr, V, Nb, etc., are sufficiently dissolved in a solid solution form, in the Ni-containing steel contemplated in the present

invention, the amount of the oxide on the surface of the slab is increased, which finally results in the occurrence of a surface flaw after the rolling. Further, heated austenite grains are coarsened, and it becomes difficult to refine the austenite grains in the subsequent rolling, which is causative of a lowering in the toughness. For these reasons, the heating temperature of the slab is limited to 1000 to 1250°C.

[0027] The heated slab is then hot-rolled at a temperature of the Ar' transformation point and air-cooled. In the steel of the present invention, since the Ar' point is as low as 400°C, the above requirement can be met by simply subjecting the heated slab to conventional hot rolling. Further, since the steel of the present invention has a composition having a sufficiently high quenchability, air cooling alone suffices for the formation of a martensitic single phase structure including a sufficiently large amount of dislocation. It is noted that, since non-diffusion type reverse transformed γ grains contributing to strengthening are the same as the γ grains after the hot rolling, if it is necessary to ensure a higher low-temperature toughness, although a lowering in the roll finishing temperature is preferred according to need for the purpose of refining the γ grains by rolling-recrystallization, there is no limitation on the method.

[0028] The steel plate after hot rolling and air cooling is then reheated to a temperature range of from (A_{c3} point - 40°C) to (A_{c3} point + 40°C) and quenched. In the step of heat treatment, wherein reheating is effected with the martensite structure used as a precursor structure, when the steel is heated to an α-γ dual phase coexisting temperature region, diffusion type reverse transformed γ grains comprising an ordinary massive austenite are formed from old austenite grain boundaries while a group of acicular austenites are formed from the intragranular martensite. They coexist together with carbides and ferrite. Since the acicular austenite is produced by non-diffusion type (martensitic) reverse transformation, it has a large amount of dislocation that contributes to an increase in the strength. Further, the heating of the steel plate to a temperature range of from (A_{c3} point - 40°C) to (A_{c3} point + 40°C) causes the group of acicular austenites to increase their area to form non-diffusion type reverse transformed γ grains that are stably maintained up to a high temperature and become fine austenite grains comprising a mixture thereof with diffusion type reverse transformed γ grains. When quenching is effected from this temperature region, a martensitic structure, into which further dislocation has been introduced, is formed, so that it becomes possible to produce an extra high tensile steel.

[0029] When the steel plate is heated to a temperature of (A_{c3} point + 40°C), the non-diffusion type reverse transformed γ grains contributing to strengthening after quenching are converted to ordinary diffusion type reverse transformed γ grains, which gives rise to a lowering in the strength of the steel plate. Therefore, the reheating temperature for quenching should be in the range of from (A_{c3} point - 40°C) to (A_{c3} point + 40°C) and is preferably A_{c3} point $\pm$ 20°C from the viewpoint of stabilizing the non-diffusion type reverse transformed γ grains. The above-described change in the austenite grains (γ grains) is shown in Fig. 3. Fig. 3 (B) is a schematic view of a grain mixture of non-diffusion type reverse transformed γ grains with diffusion type reverse transformed γ grains, which grain mixture has been formed by a treatment in a reheating temperature region for quenching of from (A_{c3} point - 40°C) to (A_{c3} point + 40°C) specified in the present invention. Fig. 3 (A) is a diagram showing the results for a reheating temperature region of (A_{c3} point - 40°C) or below, and Fig. 3 (C) is a diagram showing the results for a reheating temperature region of (A_{c3} point + 40°C) or above.

[0030] A temperature rise rate of 120°C/min or less during the reheating is also one of the characteristic features of the present invention. Fig. 2 shows the results of a yield strength test on a steel plate produced by subjecting a slab having a composition of 0.06% C - 9.9% Ni - 1.0% Mo - 0.1% V to heating at 1150°C, rolling and air cooling, reheating the steel plate to 790°C with varied temperature rise rate, quenching the steel plate and temperature the quenched steel plate at 540°C. It is apparent that the strength is improved with lowering the temperature rise rate. It is reported that the non-diffusion type reverse transformed γ is generally formed by rapid heating. However, it has been found that, the steel having a high Ni content according to the present invention, the non-diffusion type reverse transformed γ is formed without rapid heating and, as opposed to the conventional common knowledge, a temperature rise rate of 120°C/min or less is advantageous from the viewpoint of increasing the strength. Detailed studies on this point have revealed that carbides and nitrides of Mo, Cr, V, Nb, etc., precipitated during gradual heating increase the stability of the once formed non-diffusion type reverse transformed γ, so that the area ratio of the non-diffusion type reverse transformed γ grains contributing to strengthening is increased.

[0031] The steel plate after the reheating and quenching is then tempered at a temperature of an Ac_1 point or below. In this case, when the temperature exceeds the Ac_1 point, the strength and toughness are lowered due to the formation of unstable austenite. For this reason, the tempering temperature is limited to Ac_1 point or below for the purpose of sufficiently precipitation-strengthening through fine precipitation of Mo, Cr, V, Nb, etc., to provide a high strength and a high toughness.

[0032] The steel provided by the above-described production process has a high strength and a high toughness despite a low carbon content and an remarkably improved stress corrosion cracking resistance, particularly at the welding-heat affected zone.

EXAMPLES

[0033] Steels having compositions specified in Table 1 were produced by the melt process to provide slabs that were then used to produce steel plates having a thickness of 20 to 80 mm under production conditions according to the process of the present invention or comparative process specified in Table 2.

[0034] The mechanical properties of these base materials and the K_{ISCC} value (limiting fracture toughness value relative to stress corrosion cracking resistance) of the base material portion and welding-heat affected zone were examined. The welding was effected at a heat input of 25 kJ/cm by TIG welding.

[0035] The mechanical properties of base materials produced by using plates having chemical compositions specified in Table 1 and production conditions specified in Table 2 and the results of K_{ISCC} test for the base material portion and welding-heat affected zone using test pieces specified in ASTM E 399 in artificial sea water of 3.5% NaCl are given in Table 3. In the evaluation method, a precracked test piece was used under a service environmental condition (in this case, sea water), and the tip of the notch is brought to a severe condition (stress load) to facilitate the occurrence of a delayed fracture. The stress corrosion cracking resistance is evaluated by effecting a constant load test under this environment at a K value (a coefficient of stress necessary for preventing the occurrence of cracking at the tip of the notch) on various levels to determine a limit of K_{ISCC} value that does not cause a fracture at a certain K value or less. With respect to the evaluation of the K_{ISCC} property of the welding-heat affected zone, a notch is provided at the center of HAZ as shown in Fig. 5.

[0036] In the table, the thick underlined portion is outside the scope of the present invention and unsatisfactory in the properties thereof.

Table 1

(wt.%)

	Steel	C	Si	Mn	Ni	Mo	Cr	V	Al	Cu	Nb	Ti	Ca	REM	P	S	N	O	Ac_3 (°C)
Steel of Invention	A	0.06	0.08	0.58	8.7	1.05	0.76	0.06	0.036	-	-	-	-	-	0.004	0.001	0.0032	0.0020	773
	B	0.07	0.02	0.60	8.5	1.54	0.39	0.09	0.075	-	-	-	-	-	0.002	0.002	0.0018	0.0015	785
	C	0.07	0.06	0.38	9.3	0.63	0.85	0.14	0.028	-	-	-	-	-	0.004	0.001	0.0045	0.0023	792
	D	0.06	0.04	0.55	9.7	1.20	0.55	0.10	0.032	-	-	-	-	-	0.003	0.002	0.0030	0.0018	785
	E	0.04	0.05	0.40	9.8	1.02	1.47	0.06	0.036	-	-	-	-	-	0.004	0.002	0.0045	0.0026	776
	F	0.05	0.03	0.25	9.9	1.01	0.78	0.12	0.032	-	-	-	-	-	0.001	0.001	0.0022	0.0025	760
	G	0.05	0.02	0.05	10.2	1.29	0.87	0.11	0.021	-	-	-	0.0024	-	0.001	0.001	0.0046	0.0018	768
	H	0.04	0.01	0.54	8.4	1.25	0.45	0.09	0.032	1.20	-	-	-	-	0.003	0.001	0.0025	0.0012	784
	I	0.05	0.07	0.43	9.5	0.73	1.15	0.10	0.025	0.35	-	0.008	-	0.0052	0.003	0.003	0.0035	0.0022	770
	J	0.09	0.01	0.03	10.8	1.03	0.51	0.09	0.036	0.25	0.04	-	-	-	0.003	0.002	0.0024	0.0014	761
	K	0.08	0.05	0.11	9.6	0.99	0.64	0.03	0.028	-	0.11	-	-	0.0041	0.002	0.001	0.0035	0.0015	755
	L	0.07	0.02	0.24	9.9	0.64	0.99	0.11	0.024	-	0.02	-	-	-	0.001	0.001	0.0033	0.0023	780
	M	0.06	0.06	0.52	9.8	0.95	0.57	0.06	0.067	-	0.01	-	0.0035	-	0.003	0.003	0.0024	0.0021	796
	N	0.05	0.04	0.61	9.5	1.28	0.43	0.03	0.041	-	0.04	-	-	-	0.002	0.002	0.0027	0.0018	785
	O	0.08	0.07	0.46	10.1	1.33	0.56	0.05	0.018	-	-	0.015	-	-	0.002	0.003	0.0040	0.0025	758
Comp. Steel	P	0.06	0.07	0.47	8.2	0.12	0.95	0.12	0.026	-	-	-	-	-	0.003	0.002	0.0042	0.0023	786
	Q	0.07	0.01	0.13	9.7	0.82	0.43	0.01	0.033	-	-	-	-	-	0.002	0.002	0.0019	0.0038	776
	R	0.07	0.09	0.53	4.5	1.25	0.47	0.09	0.036	-	-	-	-	-	0.003	0.001	0.0035	0.0026	814
	S	0.09	0.08	0.78	10.3	1.04	0.86	0.11	0.028	-	0.02	-	-	-	0.001	0.002	0.0027	0.0018	756
	T	0.11	0.05	0.82	9.4	1.21	0.52	0.10	0.045	-	-	-	-	-	0.002	0.001	0.0028	0.0021	764
	U	0.11	0.02	0.52	11.4	0.86	0.78	0.04	0.029	-	0.04	-	-	-	0.005	0.001	0.0027	0.0019	760
	V	0.12	0.09	0.28	9.7	1.22	0.76	0.09	0.034	-	0.03	-	-	0.0051	0.001	0.001	0.0036	0.0025	769

Note) Ac_3 transformation point was measured with a Formaster thermal expansion transformation measuring apparatus.

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Table 2

	Production Condition No.	Heating-Rolling Conditions		Reheating and Quenching Conditions		Tempering Condition
		Slab Heating Temp. (°C)	Roll Finishing Temp. (°C)	Heating Rate (°C/min)	Reheating Temp. for Quenching (°C)	Tempering Temp. (°C)
Invention	1	1100	815	35	790	550
	2	1050	900	35	800	560
	3	1230	950	80	775	550
	4	1100	800	50	790	540
	5	1050	835	10	765	540
	6	1180	850	102	770	560
	7	1200	800	78	780	540
	8	1150	820	45	785	560
	9	1150	810	30	780	550
	10	1180	850	102	770	560
	11	1150	900	42	765	550
	12	1170	950	30	790	500
	13	1200	835	15	775	560
	14	1050	825	10	790	540
	15	1000	870	8	760	560
Comparative	16	1100	840	32	775	560
	17	1200	800	78	780	540
	18	1150	825	25	820	590
	19	1150	900	42	765	550
	20	1100	805	32	790	580
	21	1180	850	102	770	560
	22	1200	800	78	780	540
	23	1100	815	190	790	540
	24	1150	835	50	700	560
	25	900	780	15	790	560
	26	1050	825	26	840	560
	27	950	760	100	780	540
	28	1170	800	252	770	550
	29	1180	950	42	830	540

Table 3

	Production Condition No.	Steel	Plate Thickness (mm)	Tensile Test			Impact Test		Limit of K_{ISCC} of Base Material (MPa$\sqrt{m}$)	Limit of K_{ISCC} of Welding Heat Affected Zone (MPa$\sqrt{m}$)
				Yield Strength (MPa)	Tensile Strength (MPa)	Elongation (%)	vTrs (°C)	vE-70°C (J)		
Ex. of Invention	1	A	40	1103	1204	24	-150	223	155	149
	2	B	40	1113	1205	22	-170	233	167	146
	3	C	20	1121	1211	22	-160	221	164	146
	4	D	40	1126	1214	22	-170	241	186	158
	5	E	50	1116	1220	23	-160	236	167	158
	6	F	40	1106	1240	23	-170	250	177	130
	7	G	40	1098	1238	22	-180	276	164	136
	8	H	40	1126	1195	24	-150	230	174	154
	9	I	20	1137	1265	22	-150	233	164	155
	10	J	40	1140	1284	23	-160	224	161	127
	11	K	40	1120	1270	22	-150	210	186	126
	12	L	40	1114	1243	23	-160	263	155	130
	13	M	60	1125	1210	22	-170	239	167	149
	14	N	50	1110	1192	24	-170	248	186	151
	15	O	60	1126	1256	22	-160	285	161	146
Comp. Ex.	16	P	40	972	1098	24	-130	227	161	136
	17	Q	40	950	1111	22	-140	256	161	136
	18	K	40	847	936	23	-130	217	177	130
	19	S	40	1120	1231	22	-120	160	135	102
	20	T	40	1127	1230	23	-130	155	111	90
	21	U	40	1125	1240	23	-110	118	150	112
	22	V	40	1140	1232	22	-150	219	142	92
	23	D	40	1018	1147	23	-140	212	150	158
	24	D	40	994	1125	22	-120	140	164	158
	25	B	40	1051	1133	24	-120	142	146	146
	26	B	40	1024	1153	22	-150	214	127	146
	27	P	40	1065	1137	23	-180	172	136	130
	28	J	40	1047	1108	24	-160	223	142	126
	29	L	40	981	1154	22	-150	206	136	130

Note) A K_{ISCC} test piece for the base material was sampled from 1/2t portion of plate thickness and notched in the C direction. On the other hand, a test piece for the welding-heat affected zone was notched at the center of the welding heat affected zone. These test pieces were tested in 3.5 % NaCl artificial sea water.

[0037] In the examples of the present invention (1-A to 15-O wherein steels falling within the scope of the present invention is used in combination with the process of the present invention), the base materials had good mechanical properties, i.e., a high strength and a high toughness, and with respect to the stress corrosion cracking resistance as well, both the base material and welding heat affected zone had a sufficiently high K_{ISCC} value.

[0038] On the other hand, with respect to comparative examples wherein the process falling within the scope of the

present invention is used in combination with comparative steels (P to V) outside the chemical composition range specified in the present invention, in 16-P and 17-Q, since the Mo and V content are low, non-diffusion type reverse transformed γ grains are not formed and the precipitation strengthening is also small, so that the strength is unsatisfactory. In 18-R, since the Ni content is low, non-diffusion type reverse transformed γ grains are not formed, so that the strength is unsatisfactory. In 19-S and 20-T, since the Mn content and both C and Mn contents are high, the toughness and the K_{ISCC} value of the base material and the welding-heat affected zone are low. In 21-U, since the C and Ni contents are high, the K_{ISCC} value of the base material and the welding-heat affected zone are low. In 22-V, since the C content is high, the K_{ISCC} value of the welding-heat affected zone is low.

[0039] With respect to comparative examples wherein steels falling within the scope of the present invention are used in combination with comparative processes (23 to 29) outside the scope of the present invention, in 23-D and 28-J, since the temperature rise rate in the reheating for quenching is high, the non-diffusion type reverse transformed γ grains become unstable, which increases the amount of the diffusion type reverse transformed γ grains, so that the strength becomes unstable. In 24-D, since the reheating temperature for quenching is so low that a large amount of ferrite is present between the group of acicular γ grains, which gives rise to a lowering in the strength and toughness. In 25-B and 27-F, since the slab heating temperature is so low that not only coarse undissolved precipitates of carbides are present but also the precipitation strengthening is small, so that the strength and toughness are unsatisfactory. In 26-B and 29-L, since the reheating temperature for quenching is high, the diffusion type reverse transformed γ grains are formed, so that the strength is unsatisfactory. Further, in this case, the K_{ISCC} value of the base material is somewhat lowered. Fig. 4 is a graph showing the K_{ISCC} values of the steel of the present invention, comparative steel and conventional materials. From this drawing, it is apparent that the K_{ISCC} value of the steel of the present invention is on a level significantly improved over those of the conventional materials.

[0040] As described above, the composition range and process according to the present invention have enabled an extra high tensile steel having a yield strength of 1080 MPa or more and excellent in low-temperature toughness and stress corrosion cracking resistance at the welding-heat affected zone to be stably produced and supplied, so that it has become possible to significantly improve the reliability of containers and equipment used in a deep-sea environment.

Claims

1. A process for producing an extra high tensile steel having an excellent stress corrosion cracking resistance, comprises the steps of: heating a slab comprising, in terms of % by weight, 0.04 to 0.09% of C, 0.01 to 0.10% of Si, 0.05 to 0.65% of Mn, 8.0 to 11.0% of Ni, 0.5 to 1.5% of Mo, 0.2 to 1.5% of Cr, 0.02 to 0.20% of V and 0.01 to 0.08% of Al with the balance consisting of iron and unavoidable impurities, to a temperature between 1000°C and 1250°C, hot-rolling the slab at a temperature of Ar' point or above, air-cooling the rolled plate, reheating the rolled plate at a rate of 120°C/min or less to a temperature region of from (A_{c3} point - 40°C) to (A_{c3} point + 40°C), quenching the reheated plate and subsequently tempering the quenched plate at a temperature of the A_{c1} point or below.

2. A process for producing an extra high tensile steel having an excellent stress corrosion cracking resistance, comprises the steps of: heating a slab comprising, in terms of % by weight, 0.04 to 0.09% of C, 0.01 to 0.10% of Si, 0.05 to 0.65% of Mn, 8.0 to 11.0% of Ni, 0.5 to 1.5% of Mo, 0.2 to 1.5% of Cr, 0.02 to 0.20% of V and 0.01 to 0.08% of Al and further comprising at least one member selected from the group consisting of 0.2 to 1.5% of Cu, 0.005 to 0.10% of Nb and 0.005 to 0.03% of Ti as strength improving elements and 0.0005 to 0.005% of Ca and 0.0005 to 0.0100% of REM as elements having a capability of regulating the form of inclusions with the balance consisting of iron and unavoidable impurities, to a temperature between 1000°C and 1250°C, hot-rolling the slab at a temperature of Ar' point or above, air-cooling the rolled plate, reheating the rolled plate at a rate of 120°C/min or less to a temperature region of from (A_{c3} point - 40°C) to (A_{c3} point + 40°C), quenching the reheated plate and subsequently tempering the quenched plate at a temperature of the A_{c1} point or below.

Patentansprüche

1. Verfahren zur Herstellung eines hochfesten Stahls mit einer ausgezeichneten Beständigkeit gegen Spannungsrisskorrosion, umfassend die Schritte:
   Erwärmen einer Bramme, umfassend, in Gew.-%, 0,04 bis 0,09 % C, 0,01 bis 0,10 % Si, 0,05 bis 0,65 % Mn, 8,0 bis 11,0 % Ni, 0,5 bis 1,5 % Mo, 0,2 bis 1,5 % Cr, 0,02 bis 0,20 % V und 0,01 bis 0,08 % Al wobei der Rest aus Eisen und unvermeidbaren Verunreinigungen besteht, auf eine Temperatur zwischen 1000°C und 1250°C, Heißwalzen der Bramme bei einer Temperatur des Ar' Punkts oder darüber, Luftkühlen der gewalzten Platte, Wie-

dererwärmen der gewalzten Platte mit einer Geschwindigkeit von 120°C/Minute oder weniger auf einen Temperaturbereich von (A_{c3} Punkt -40°C) bis (A_{c3} Punkt +40°C), Abschrecken der wiedererwärmten Platte und anschließend Tempern der abgeschreckten Platte bei einer Temperatur des A_{c1} Punktes oder darunter.

2. Verfahren zur Herstellung eines hochfesten Stahls mit einer ausgezeichneten Beständigkeit gegen Spannungsrisskorrosion, umfassend die Schritte:
Erwärmen einer Bramme, umfassend, in Gew.-%, 0,04 bis 0,09 % C, 0,01 bis 0,10 % Si, 0,05 bis 0,65 % Mn, 8,0 bis 11,0 % Ni, 0,5 bis 1,5 % Mo, 0,2 bis 1,5 % Cr, 0,02 bis 0,20 % V und 0,1 bis 0,08 % Al und weiterhin umfassend mindestens einen Vertreter, ausgewählt aus 0,2 bis 1,5 % Cu, 0,005 bis 0,10 % Nb und 0,005 bis 0,03 % Ti als Festigkeit verbessernde Elemente und 0,0005 bis 0,005 % Ca und 0,0005 bis 0,0100 % REM als Elemente mit der Fähigkeit, die Form von Einschlüssen zu regeln, wobei der Rest aus Eisen und unvermeidbaren Verunreinigungen besteht, auf eine Temperatur zwischen 1000°C und 1250°C, Heißwalzen der Bramme bei einer Temperatur des Ar' Punkts oder darüber, Luftkühlen der gewalzten Platte, Wiedererwärmen der gewalzten Platte mit einer Geschwindigkeit von 120°C/Minute oder weniger auf einen Temperaturbereich von (A_{c3} Punkt -40°C) bis (A_{c3} Punkt +40°C), Abschrecken der wiedererwärmten Platte und anschließend Tempern der abgeschreckten Platte bei einer Temperatur des A_{c1} Punktes oder darunter.

Revendications

1. Procédé pour produire un acier à ultra-haute résistance ayant une excellente résistance à la fissuration par corrosion sous contrainte, comprenant les étapes de: chauffage d'une brame comprenant, en pourcentages en masse, 0,04 à 0,09 % de C, 0,01 à 0,10 % de Si, 0,05 à 0,65 % de Mn, 8,0 à 11,0 % de Ni, 0,5 à 1,5 % de Mo, 0,2 à 1,5 % de Cr, 0,02 à 0,20 % de V et 0,01 à 0,08 % de Al, le complément consistant en fer et en impuretés inévitables, à une température située entre 1 000°C et 1 250°C, le laminage à chaud de la brame à une température du point Ar' ou supérieure, le refroidissement à l'air de la plaque laminée, le réchauffage de la plaque laminée à une vitesse de 120°C/min ou moins jusqu'à une région de température du (point A_{c3} - 40°C) au (point A_{c3} + 40°C), la trempe de la plaque réchauffée puis le revenu de la plaque trempée à une température du point A_{c1} ou inférieure.

2. Procédé pour produire un acier à ultra haute-résistance ayant une excellente résistance à la fissuration par corrosion sous contrainte, comprenant les étapes de : chauffage d'une brame comprenant, en pourcentages en masse, 0,04 à 0,09 % de C, 0,01 à 0,10 % de Si, 0,05 à 0,65 % de Mn, 8,0 à 11,0 % de Ni, 0,5 à 1,5 % de Mo, 0,2 à 1,5 % de Cr, 0,02 à 0,20 % de V et 0,01 à 0,08 % de Al et comprenant en outre au moins un élément choisi dans le groupe consistant en 0,2 à 1,5 % de Cu, 0,005 à 0,10 % de Nb et 0,005 à 0,03 % de Ti comme éléments améliorant la résistance et 0,0005 à 0,005 % de Ca et 0,0005 à 0,0100 % de MTR comme éléments ayant une capacité de réguler la forme des inclusions, le complément consistant en fer et en impuretés inévitables, à une température située entre 1 000°C et 1 250°C, le laminage à chaud de la brame à une température du point Ar' ou supérieure, le refroidissement à l'air de la plaque laminée, le réchauffage de la plaque laminée à une vitesse de 120°C/min ou moins jusqu'à une région de température du (point A_{c3}- 40°C) au (point A_{c3} + 40°C), la trempe de la plaque réchauffée puis le revenu de la plaque trempée à une température du point A_{c1} ou inférieure.

Fig. 1

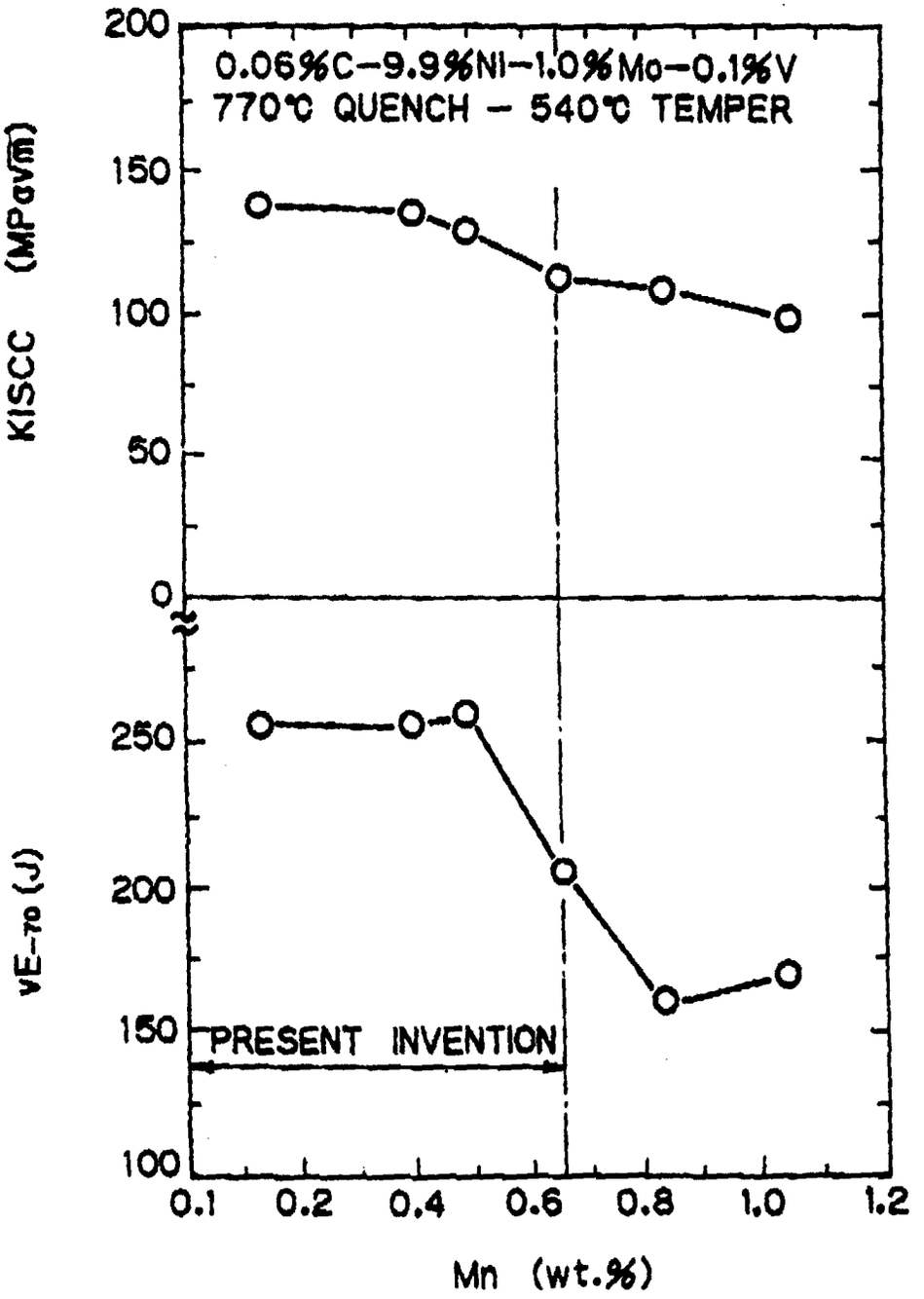

0.06%C-9.9%Ni-1.0%Mo-0.1%V
770°C QUENCH - 540°C TEMPER
KISCC (MPa√m)
vE-70 (J)
PRESENT INVENTION
Mn (wt.%)
200
150
100
50
0
250
200
150
100
0.1
0.2
0.4
0.6
0.8
1.0
1.2

Fig. 2

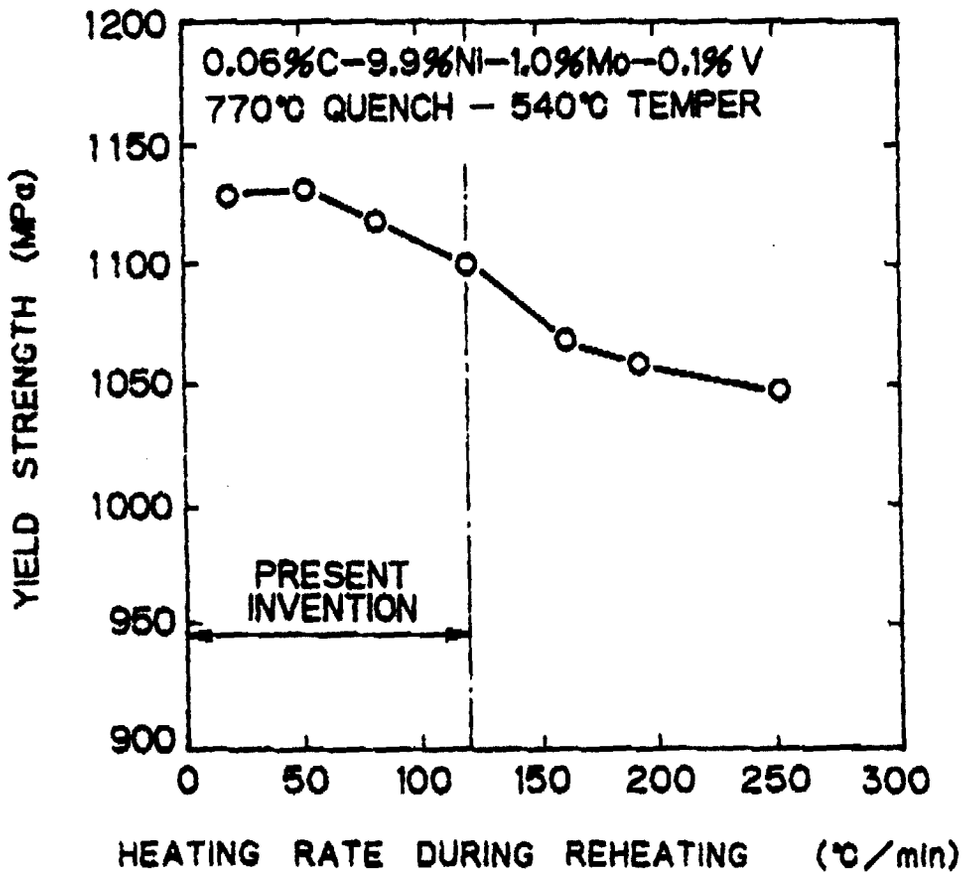

0.06%C-9.9%Ni-1.0%Mo-0.1% V
770°C QUENCH - 540°C TEMPER
PRESENT INVENTION
YIELD STRENGTH (MPa)
1200
1150
1100
1050
1000
950
900
0
50
100
150
200
250
300
HEATING RATE DURING REHEATING (°C/min)

Fig. 3A

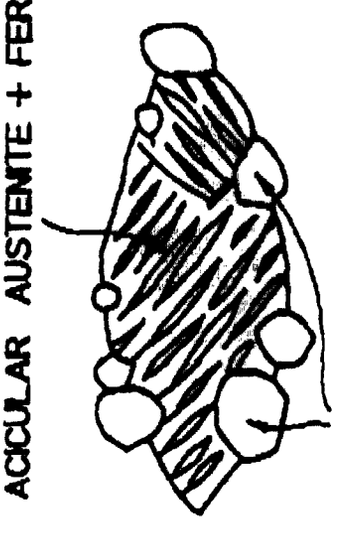


Fig. 3B

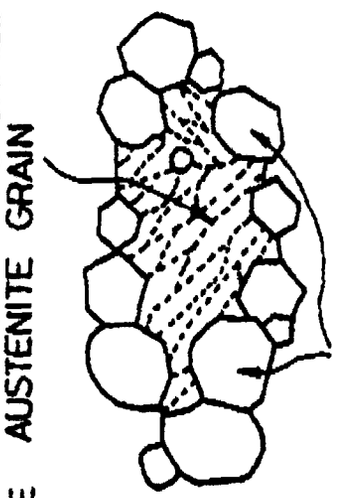


Fig. 3C

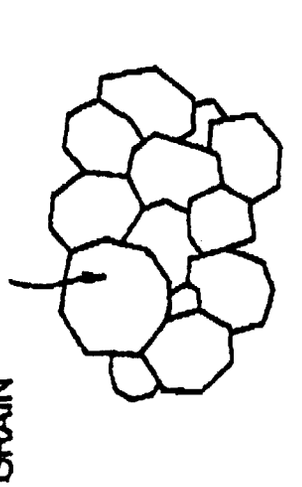


Fig. 4

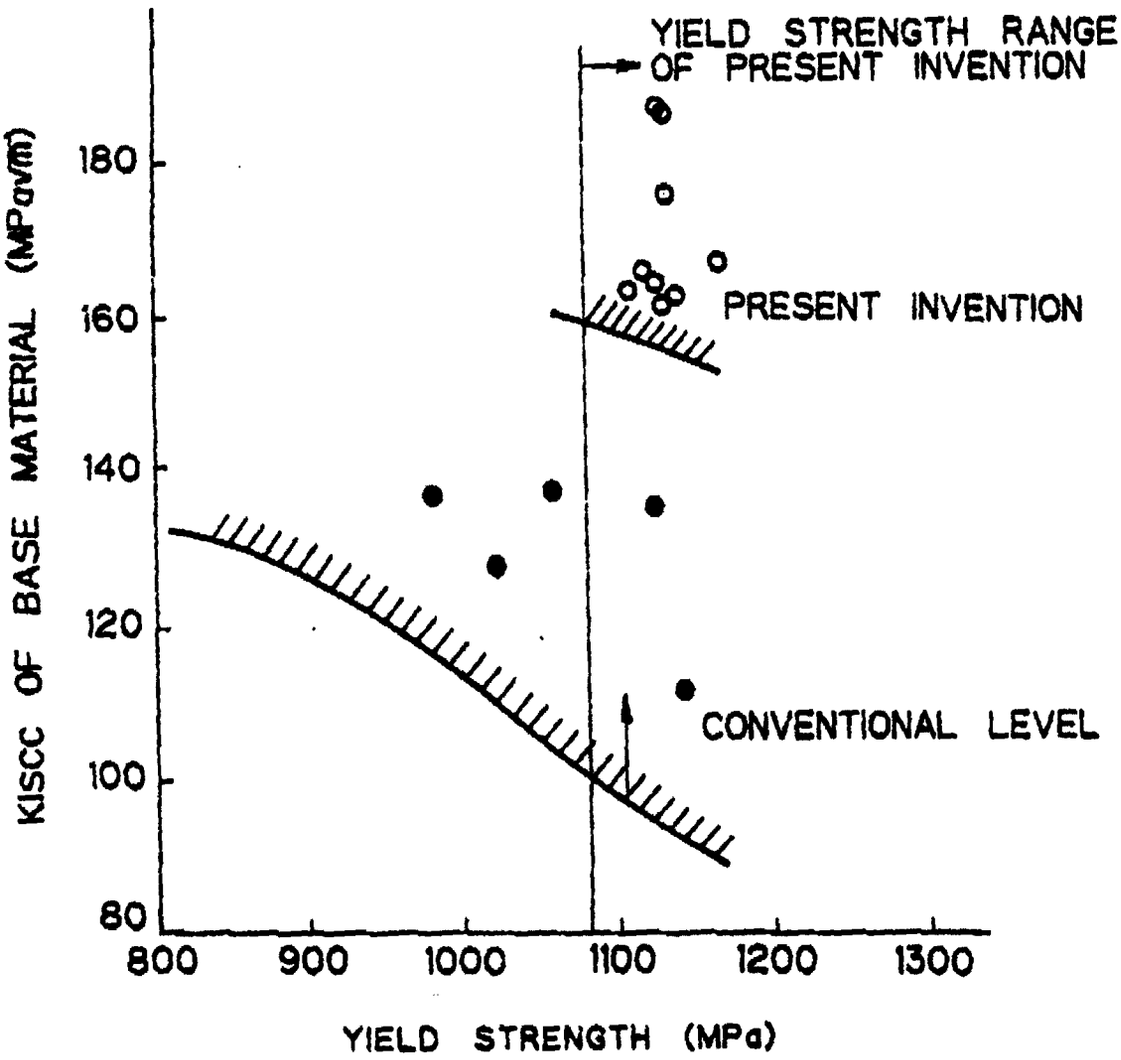

YIELD STRENGTH RANGE
OF PRESENT INVENTION
PRESENT INVENTION
CONVENTIONAL LEVEL
KISCC OF BASE MATERIAL (MPa√m)
180
160
140
120
100
80
800
900
1000
1100
1200
1300
YIELD STRENGTH (MPa)

Fig. 5

