April 3, 1973 SUSUMU SATOH ET AL 3,725,049

SEMI-KILLED HIGH TENSILE STRENGTH STEELS

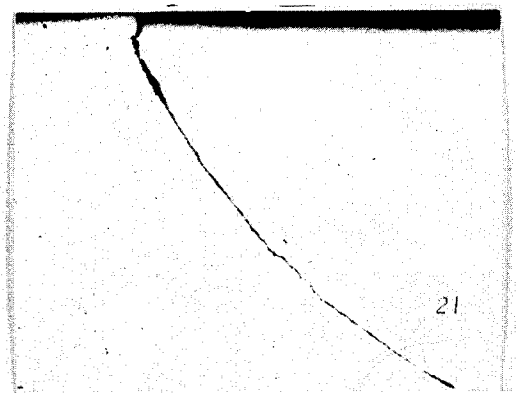
Filed Aug. 12, 1970 3 Sheets-Sheet 1

HOOK CRACK SEEN AT THE WELDED PORTION DURING PIPE PRODUCTION



FIG. 1

CROSS SECTION OF STEEL PIPE ATTACKED BY HOOK CRACK



(X 100)

FIG. 2

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SEMI-KILLED HIGH TENSILE STRENGTH STEELS

Filed Aug. 12, 1970 3 Sheets-Sheet 2

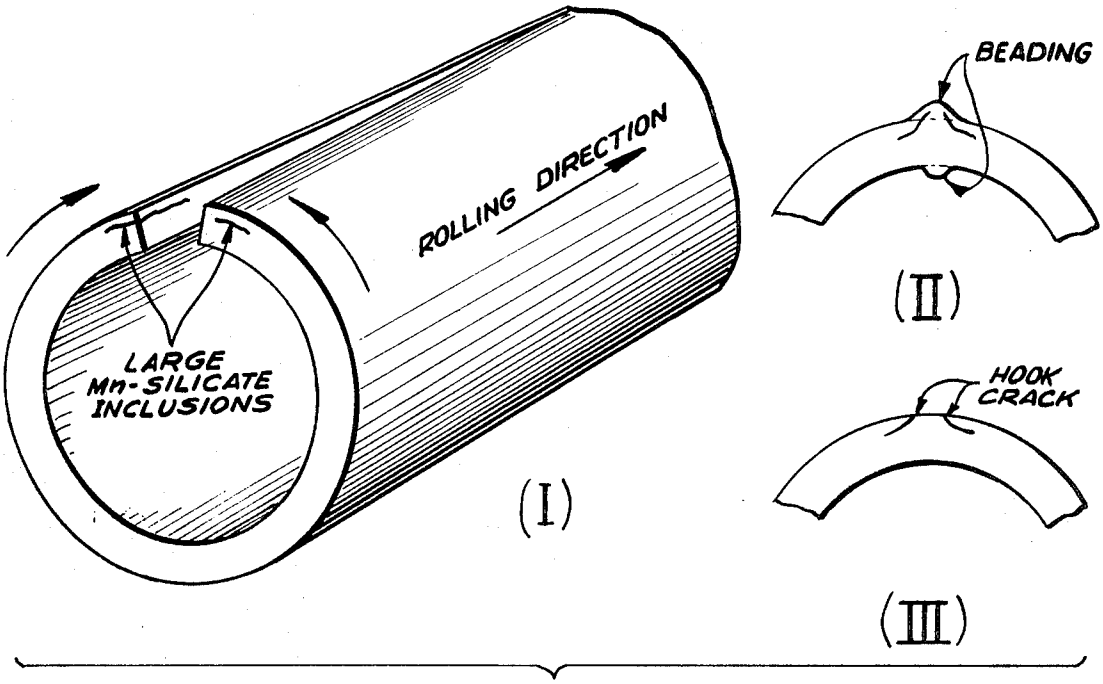


FIG. 3

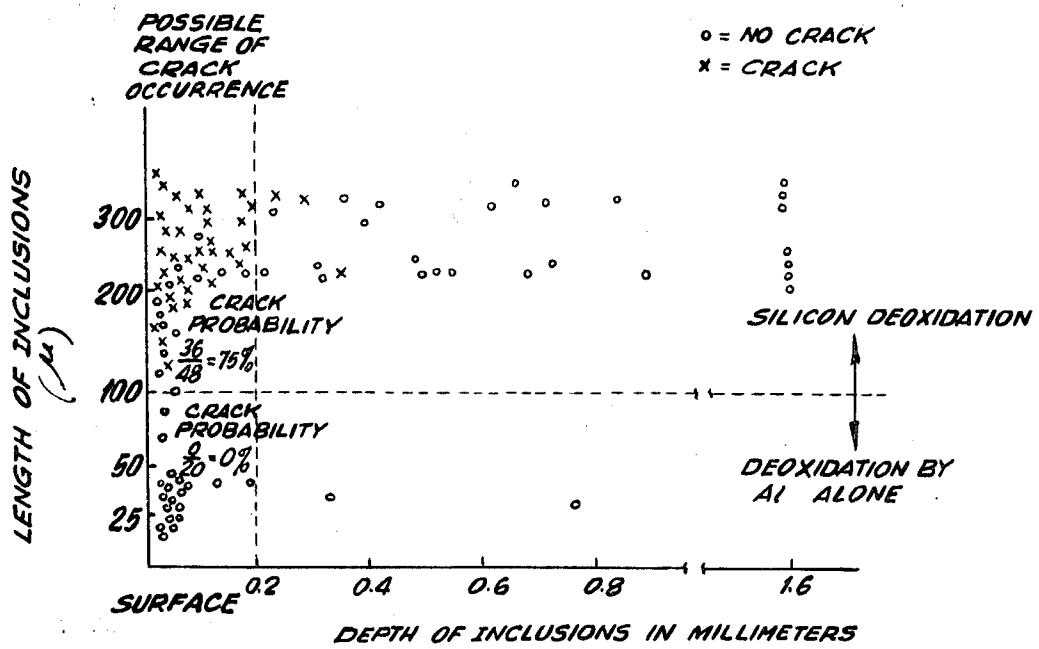
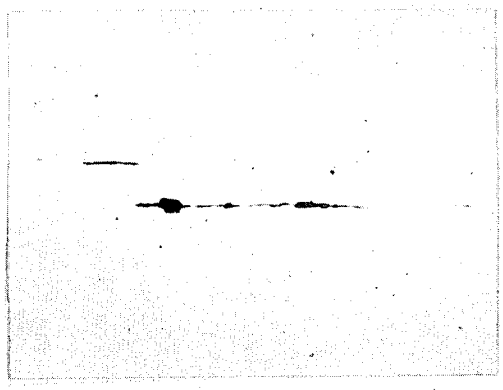


FIG. 4

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INCLUSIONS IN CB-CONTAINING SEMIKILLED STEEL DEOXIDIZED BY SILICON



(L DIRECTION, X 100)

FIG. 5 (I)

INCLUSIONS IN INVENTIVE STEEL



(L DIRECTION, X 100)

FIG. 5 (II)

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3,725,049

SEMI-SKILLED HIGH TENSILE STRENGTH STEELS

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Continuation-in-part of abandoned application Ser. No. 617,112, Feb. 20, 1967. This application Aug. 12, 1970, Ser. No. 63,307

Claims priority, application Japan, Mar. 11, 1966, 41/15,060; July 21, 1966, 41/47,892

Int. Cl. C22c *39/26, 39/54*

U.S. Cl. 75—123 D 5 Claims

ABSTRACT OF THE DISCLOSURE

Semi-killed steel composition exhibiting high tensile strength and containing manganese and at least one of the metals columbium and vanadium while being devoid of large non-metallic inclusions. The semi-killed steel composition is characterized in that it has been deoxidized by aluminum alone whereby the formation of inclusions of manganese silicate larger than 100μ is avoided. Further, the alumina inclusions formed by the aluminum deoxidation are not larger than 100μ. There is little tendency toward crack formation in articles manufactured from the instant steel composition.

CROSS-REFERENCE TO PRIOR APPLICATIONS

This is a continuation-in-part of our copending application, Ser. No. 617,112, filed on Feb. 20, 1967, now abandoned.

SUMMARY OF INVENTION

This invention generally relates to steels and is particularly directed to novel non-tempered semi-killed steel compositions exhibiting high tensile strength while being devoid of large non-metallic inclusions and containing manganese and at least one of the metals columbium and vanadium. The invention is also concerned with a process for producing the new steel compositions, the inventive steels being particularly suitable for use in the manufacture of steel plates and pipes. An essential characteristic of the novel semi-killed steels is that they have been deoxidized by aluminum alone.

It has previously been suggested to produce non-tempered, high tensile strength steel by adding suitable amounts of columbium and/or vanadium to semi-killed steel. The semi-killed steel to which columbium and/or vanadium are added in accordance with the prior art procedures is, without exception, deoxidized by silicon or by silicon and aluminum. No prior art columbium and/or vanadium containing high tensile strength semi-killed steel is known in which the deoxidation is carried out in the absence of silicon and by aluminum alone.

Conventional semi-killed high tensile strength steel plates containing columbium and/or vanadium are used for various purposes as, for example, in the manufacture of pipe lines for conveying oil and the like fluids, in the manufacture of motor car frames and the like.

The production of pipes from such conventional steel is, however, fraught with difficulties due to crack defects which tend to occur in the pipes. These crack defects, generally referred to in the art as hook cracks, are frequently formed in the welded portion, a fact which of course, lowers the yield.

In respect to frames and other structural members formed from such conventional steel plates, again cracks frequently occur at the corners upon bending of the plates by 90°.

Extensive investigations have been carried out and tests have been performed by the present inventors with a

view to ascertaining and pinpointing the causes for these crack defects which occur upon working of steel plates made from the conventional prior art steels of the indicated kind. These investigations and tests have established the following facts: If a semi-killed steel is produced by deoxidizing the heat in the furnace, ladle or mold with silicon or silicon and aluminum, large silicate inclusions are formed which are not uniformly distributed throughout the heat and thus the solidified ingot, but which have a tendency to lodge themselves in the skin portion of the ingot. Consequently, when the ingot is hot rolled, these relatively large inclusions are stretched or elongated in the rolling direction and appear in the final steel product in the form of manganese silicate inclusions near the surface of the product. It has been established that the hook cracks previously referred to and occurring during pipe line production and the crack defects formed during bending in frame production, are due to the presence of these relatively large manganese silicate inclusions.

Steel pipes, particularly electrically welded steel pipes, are normally produced as follows: Generally, hot coil steel is formed into a pipe by a pipe mill and welded together, whereupon the welding seam or joint is subjected to various severe examinations and tests such as supersonic inspection for the purpose of detecting defects in the welded portions. These examinations also include hydrostatic testing, flat testing, expansion testing and the like.

In the accompanying drawings:

FIG. 1 is a photographic rendering showing hook cracks which occurred at the welded portion during pipe production;

FIG. 2 is a photographic rendering showing a cross section of the welded portion in which the hook crack developed during pipe production, the hook crack being shown in 100× magnification;

FIG. 3(I), (II) and (III), respectively, shows the development of hook cracks;

FIG. 4 is a graph indicating the relationship between the bending quality and inclusions in carbon semi-killed steel plates deoxidized by aluminum and by silicon, respectively; and

FIG. 5(I) is a photographic rendering showing inclusions in the rolling direction (L direction) in a conventional columbium-containing steel, while FIG. 5(II) is a photograph showing corresponding inclusions in the L direction in a steel in accordance with this invention, both FIG. 5(I) and FIG. 5(II) being shown in 100× magnification.

A hook crack is a kind of hairline crack which appears in the bead of a pipe extending lengthwise of the pipe, as seen in FIG. 1. When this defective portion of a pipe is cut transverse to the lengthwise direction of the pipe and viewed under a microscope, it is noted that the defective portion contains relatively large inclusions of manganese silicate of more than 100μ in length, the crack ocurring along these manganese silicates as apparent from FIG. 2.

The following conclusions can be reached from the above observations in respect to the causes for the hook crack formation:

In respect to conventional semi-killed steels containing columbium and/or vanadium in which the steel has been deoxidized by silicon alone or by silicon and aluminum, the manganese silicate inclusions, during the plate rolling, are present near the surface of the plate in the manner shown in FIG. 3(I). Due to the presence of these manganese silicate inclusions of relatively large size, the steel mass immediately adjacent and enveloping the inclusions is subjected to larger stress forces during bending and pressure welding than the remaining steel mass. Therefore, the strata immediately below the surface of the plate are

prone to crack formation, the cracks developing from the surface of the plate to the location of the inclusions whereupon the cracks proceed along the inclusions. A fresh crack oftentimes occurs from the metal mass adjacent the inclusion and extending toward and into the centrally located inner portion of the metal.

FIG. 3(II) illustrates the conditions in respect to a bead obtained by resistance welding in which the metal is shown to flow. As indicated in FIG. 3(III) the bead is removed by the bead cutting operation after welding and a crack appears in the bead region when the bead is cut away due to the presence of large inclusions, the crack being in the nature of a hook crack.

As previously set forth, if a columbium and/or vanadium-containing steel plate which has been deoxidized in the conventional manner by silicon or silicon and aluminum is pressure-bent into a motor car frame or the like, cracks have a tendency to occur in the corner portions of the pressed material. The mechanism causing the crack formation is very similar to that of the hook crack formation as explained above in the forming of plates into pipes. Large manganese silicate inclusions which are located adjacent the surface of the steel plate or sheet are subjected to considerable stress during the press working and become a stress-concentration source.

It is thus clear that the causes for the hook cracks in the welded portion of pipe lines and the cracks occurring during bend working of frames must be attributed to the large manganese silicate inclusions which are present in the conventional steel plates or sheets near the surface thereof.

These phenomena can also be observed during the working of an ordinary plain carbon semi-killed steel plate. However, the crack formation is more pronounced in a high tensile strength steel plate enriched with columbium and/or vanadium, because the stresses to which the sheet is subjected during the working are much larger. The formation of the cracks referred to is well known in the industry and is a dreaded phenomenon which has not been solved and overcome prior to the invention in spite of serious efforts in this direction. The formation of these cracks renders a large proportion of manufactured pipes or frames defective which, of course, significantly lowers the production yield.

Accordingly, it is a primary object of the invention to overcome the drawbacks and disadvantages of prior art high tensile strength steels containing columbium and/or vanadium and to produce steel of the indicated kind which can be worked into pipes and bent into frames and the like structural members without risk of crack formation.

Another object of the invention is to provide a steel composition of the indicated kind which is devoid of alumina and manganese silicate inclusions larger than 100μ.

It is also an object of this invention to produce semi-killed high tensile strength steel of the indicated nature which has superior characteristics in many respects as compared to prior art steels.

Still another object of the invention is to provide an improved process for manufacturing high tensile strength steel of the indicated kind.

It is also an object of this invention to produce novel columbium and/or vanadium-containing high tensile strength steels which can be readily worked into pipes or structural members with a high production yield.

Generally, it is an object of this invention to improve on the art of high tensile strength semi-killed steels as presently practiced.

From the above it will be apparent that, with a view to eliminating crack formations of the indicated kind, it is necessary to reduce or prevent the formation of large manganese silicate and alumina inclusions within the steel mass.

Theoretically, this could possible be accomplished in the following two manners:

(1) The deoxidation degree could be intensified so as to prevent secondary deoxidation reactions within the mold.

(2) To reduce the size of the inclusions by varying or altering the nature of the deoxidizing agents without, however, increasing the deoxidation degree.

In respect to alternative 1 above, it should be noted that in respect to semi-killed steels of a customary degree of deoxidation, in which the deoxidation is accomplished by silicon alone or by silicon and aluminum, the oxygen concentration in the molten steel to be poured into a mold is not sufficiently decreased so as to avoid a secondary deoxidation reaction with the silicon. In fact, such secondary reaction takes place as the temperature of the molten steel decreases and during the solidification, resulting in the formation of a considerable amount of manganese silicate which thus remains in the solidified ingot in the form of inclusions. Therefore, if silicon deoxidation is performed, it is extremely difficult, if not impossible, to prevent secondary deoxidation in the mold within the deoxidation range of semi-killed steel.

Consequently, if the deoxidation is carried out with silicon and large manganese silicate inclusions are to be avoided in the steel ingots, it is necessary to increase the silicon addition to the furnace or the ladle so as to completely kill the molten steel and prevent the occurrence and progress of secondary deoxidation reactions due to the presence of silicon. However, if this is done, considerable pipe formation takes place in the semi-killed steel in the top portion of the steel ingot which in turn negates the specific advantage of semi-killed steel, to wit, the attainment of higher yields. For this reason, it is not practically feasible to reduce the large inclusions near the surface of the steel plate while at the same time attaining a deoxidation degree with the deoxidation range for ordinary semi-killed steels. In practice, the avoidance of the large inclusions would therefore at the same time result in a killed steel.

Referring now to alternative 2, as mentioned above, the inclusions which are formed in the silicon deoxidation are large-sized manganese silicates, while by contrast in deoxidation carried out with aluminum alone, any inclusions which are formed consist of alumina (Al_2O_3) and heroynite ($FeO\ Al_2O_3$). Such alumina or heroynite inclusions are much finer and of smaller size than manganeses silicates. FIG. 5(I) shows inclusions as they occur in a conventional semi-killed steel plate containing columbium and/or vanadium, the steel having been deoxidized by silicon or silicon and aluminum, while FIG. 5(II) shows inclusions in an inventive semi-killed steel plate containing columbium and/or vanadium, wherein the deoxidation has been carried out with aluminum alone. For the reasons advanced, and even if inclusions appear at a similar position near the surface, as do the manganese silicates in the conventional steels, these inclusions do not materially affect the stress conditions and no stress concentration takes place. Accordingly, since the inclusions are of much smaller size and do not exceed 100μ as seen in FIG. 4, no cracks are formed during the forming into pipes or bending of the plates into frame structures.

The fact that finer inclusions do not result in stress concentrations near the surface of the plate but that stresses are substantially uniformly distributed is illustrated in FIG. 4. The graph shows that 75% of the cracks occur when a steel plate of 3.2 mm. (0.125 inch) is bent 90° during a laboratory bending test, if large manganese silicates are present at a depth within 0.2 mm. (0.008 inch) from the surface. By contrast, no cracks could be observed in the presence of the small alumina inclusions formed by the deoxidation with aluminum alone.

It has been established from the above observations that deoxidation carried out with aluminum without sili-

con yields significantly more advantageous results if proceeding according to alternative 2 above than if the deoxidation is carried out with silicon or with silicon and aluminum.

For the reasons advanced, alternative 1 referred to above is impractical, if a semi-killed steel is to be produced, while the deoxidation with aluminum alone in accordance with alternative 2 yields excellent results. For this reason, the present invention proceeds according to alternative 2, the deoxidation being carried out with aluminum alone.

However, if proceeding in this manner, to wit, if the deoxidation is carried out with aluminum, the control of the deoxidation reaction is somewhat more difficult than when deoxidation is carried out in the presence of silicon. Therefore, care must be taken in practicing the inventive process so as to make sure that during the deoxidation no large pipe formation occurs in the ingot.

Briefly, and in accordance with the invention, a novel non-tempered high tensile strength steel is therefore produced by adding columbium and/or vanadium to a semi-killed manganese-containing steel which has been prepared by the deoxidation with aluminum alone. It should be emphasized that deoxidation by aluminum alone has not previously been attempted in connection with steels of the indicated nature.

Extensive tests have established that best results are achieved if the aluminum content in the final steel composition does not exceed 0.02%, calculated as acid soluble aluminum. The reason for this limitation is that a low content of aluminum is sufficient in an aluminum deoxidized semi-killed steel as contrasted to an aluminum killed steel in which the aluminum is added for the purpose of regulating the grain size. Thus the upper limit for the aluminum content according to this invention is about 0.02%.

In respect to the other alloying elements of the steel, the following should be observed:

The carbon content of the steel should be in the range of between about 0.06 to 0.30%, because a carbon content in an amount lower than 0.06% would be insufficient to provide the required high tensile strength. On the other hand, carbon in excess of 0.30% lowers the elongation, drawability and impact value characteristics as well as the weldability. Higher carbon contents would, of course, increase the strength, but for the purposes of the present invention the other characteristics hereinabove referred to are more important. For this reason, it is desirable to maintain the carbon content as low as possible and the indicated range of 0.06 to 0.30 has proved to be most successful.

If the carbon content exceeds 0.30%, the ductility toughness deteriorates and the weldability is lowered and thus the upper limit of the carbon content should not exceed 0.30%.

Manganese is a useful element for increasing the strength as well as the impact value characteristics. However, amounts of less than 0.30% of manganese do not give sufficient strength in the same manner as to low a carbon content lowers the strength value. Manganese in an amount exceeding 1.5%, however, causes deterioration of the impact value and the weldability. Thus, the manganese range should be within 0.30 to 1.50%.

The columbium content should be 0.005 to 0.1% while the vanadium content is limited to 0.02 to 0.4% to obtain high tensile strength steel plates having 40 to 65 kg. per mm.^{2} (56.900 to 92.500 p.s.i.) tensile strength, and 25 to 52 kg./mm.^{2} (35.000 to 94.000 p.s.i.) yield strength as hot rolled A columbium content of less than 0.005% and a vanadium content lower than 0.02% would not be effective for increasing the strength of the product, while on the other hand columbium in excess of 0.1% and vanadium in excess of 0.04% does not result in any significantly increased strength.

The optimum columbium and vanadium contents in the steel depend, of course, on the carbon and nitrogen contents in the steel. However, it has been ascertained that in respect to a low carbon steel containing a customary amount of nitrogen (0.002 to 0.01%), the best results in respect to strength of the product are obtained if the columbium content is within the range of 0.01 to 0.06% with the vanadium content being within the range of 0.05 to 0.30%. The columbium is advantageously added in the form of Fe-Cb alloy such as, for example, plain Fe-Cb or Fe-Cb-Al. The columbium addition in this form is made to the ladle or the mold.

The vanadium is preferably added to the ladle or mold in the form of Fe-V or as Fe-V alloys with other elements, to wit, aluminum (Fe-V-Al).

As previously set forth, no silicon is used as deoxidizer since silicon is the main cause for the undesired manganese silicate inclusions. Therefore, any silicon which may be present in the steel is derived from unavoidable contaminations and impurities during the steel making. No positive silicon addition is effected. The upper limit of the silicon content in the steel should not exceed 0.02%.

Depending on the use to which the steel is to be put and on the requirements for the steel, other elements may optionally be added, such as, for example, copper phosphorus and chromium. Copper is a relatively cheap element effective for obtaining desired strength and for increasing atmospheric resistance. On the other hand, relatively large addition of copper tends to cause cracks during hot rolling, thus rendering production diffcult. For this reason, it has been established that the copper content should not exceed 0.5%.

In respect to phosphorus, this element, particularly in conjunction with copper, is effective for increasing atmospheric resistance but, again, excessive amounts of phosphorus negatively affect workability at room temperature. It has been established that the phosphorus content should not exceed 0.10%.

Chromium is effective for increasing the tensile strength and when present in conjunction with copper is effective for increasing atmospheric resistance. The optimum content of chromium should not exceed 1.00%.

Pursuant to the invention, steel containing the above elements in specified amounts is rolled or formed into ingots or billets or the like shapes and then is hot rolled in customary manner. The steel is heated at a temperature of above 1160° C. (2120° F.) for two to six hours and hot rolled at a final finishing temperature of between about 750 to 900° C. (1380 to 1652° F.) and coiled at a temperature between about 350 to 700° C. (660 to 1292° F.) Heating to above 1160° C. causes columbium and vanadium to dissolve into austenite and to form precipitates which cohere to the matrix after the hot rolling, thus strengthening the steel. Therefore, the desired properties are obtained by combination of the above heating temperature, final finishing temperature and coiling temperature according to the requirements as to the strength or ductility rather than strength.

No large-sized manganese silicate inclusions are formed in the present steel since silicon is not employed as deoxidizer, deoxidation being carried out by the aluminum. The only inclusions which can be observed in the present steel are fine spherical Al_2O_3 particles of a size less than 100μ. Therefore, no hook cracks occur in the welded portions of steel pipes produced from the steel and no cracks or failure takes place during bending operations. Consequently, the present invention completely eliminates the difficulties previously met with conventional semi-killed high tensile strength steels containing columbium and/or vanadium in which the deoxidation is carried out with silicon or silicon and aluminum. The present invention makes possible the production of a semi-killed high tensile strength steel plate containing columbium and/or vanadium with excellent workability.

The steel plate produced according to the present invention exhibits superior toughness, particularly in the right angle direction to its rolling direction, as will become apparent more clearly from the following Example 1. This is due to the fact that in the ordinary prior art semi-killed steel plates large manganese silicates are present in the rolling direction and thus orientation is pronounced while, by contrast, in the steel plate produced according to the present invention the inclusions of fine and non-oriented alumina Al_2O_3 particles increase the toughness.

The invention will now be described by several examples, it being understood, however, that these examples are given by way of illustration and not by way of limitation and that many changes may be effected without affecting in any way the scope and spirit of the invention as recited in the appended claims.

EXAMPLE 1

The following ingot making conditions for steel (convertor steel) produced according to the present invention prevailed:

Ladle analysis in percent: C, 0.16; Si, 0.01; Mn, 0.47; P, 0.010; S, 0.016.
Amount of Al for ladle deoxidation: 320 g./t. (0.700 lb./t.)

Amount of Al for mold dexidation:
Mold No. 3: 121 g./t. (0.270 lb./t.)
Mold No. 4: 115 g./t. (0.255 lb./t.)
Mold No. 5: 115 g./t. (0.255 lb./t.)
Mold No. 6: 110 g./t. (0.240 lb./t.)
Tapping temperature: 1610° C. (2930° F.)
Ingot weight: 14,400 kg.

After the molten steel was poured from the ladle into the molds, Fe-Cb (Cb 61.0%) was added to the heat of Molds Nos. 4, 5 and 6. The addition of Fe-Cb was started 10 seconds after the beginning of pouring and continued uniformly up to the completion of the pouring. Fe-Cb was crushed into particle size of less than 10 mm. (0.39 inch) and added in amounts tabulated below. Fe-Cb was added into Molds Nos. 4, 5 and 6 in an amount of ⅓ kg./t. (0.730 lb./t.), 1 kg./t. (2.20 lb./t.) and 1.5 kg./t. (3.30 lb./t.), respectively.

Mold No. 3 contained comparison steel to which no Fe-Cb was added.

The steel ingots thus obtained were subjected to breaking down rolling into slabs which latter were heated at 1260° C. (2300° F.) and rolled into plates of a thickness of 6.0 mm. (0.236 inch) by a continuous hot rolling mill under the same conditions: Final finishing temperature: 840° C. (1550° F.) and coiling temperature: 600° C. (1110° F.). The chemical compositions and mechanical properties of the steel plates thus produced are shown in Table 1. The tension test results as shown in Table 1 (as well as in Tables 2, 4, 5, 14 and 17) were obtained in the rolling direction, and test pieces were taken in the rolling direction. The standard distance of elongation was 50 mm. (2 inches) (the test pieces for the results tabulated in Tables 2, 4, 5, 11, 14, 17 and 20 were made in the same manner). The specimens for impact tests were taken at right angle to the rolling direction and had a size of 5 x 10 x 55 mm. (0.197 x 0.394 x 2.17 inches). They were tested with 2 mm. (0.079 inch) V notch at 0° C. (32° F.). (The same procedures were followed in the tests tabulated in Tables 2, 4, 5, 11, 14, 17 and 20.)

TABLE 1

Mold No.	Fe-Cb addition, kg./t.	Chemical composition (percent) C	Si	Mn	Cb	Sol. Al
3	0	0.17	0.01	0.48	----------	0.011
4	⅓	0.16	0.01	0.48	0.009	0.010
5	1	0.17	0.01	0.47	0.032	0.009
6	1½	0.17	0.01	0.48	0.047	0.006

TENSION TEST RESULTS

Mold No.	Fe-Cb addition, kg./t.	T.S., kg./mm.² (p.s.i.)	Y/P., kg./mm.² (p.s.i.)	Elongation, percent	Impact value, kg./m. (ft.-lb.)
3	0	43.6 (62,000)	31.4 (44,700)	39.7	3.9 (28.1)
4	⅓	47.1 (67,000)	37.2 (52,900)	33.1	3.7 (26.5)
5	1	53.7 (76,400)	43.0 (61,200)	30.6	3.4 (24.5)
6	1½	58.9 (83,800)	47.9 (68,130)	27.7	3.0 (21.6)

By contrast, ingot making conditions for steel (convertor steel) according to the conventional procedure are as follows:

Ladle analysis in percent: C, 0.15; Si, 0.05; Mn, 0.48; P, 0.012; S, 0.014.
Ladle deoxidation: Fe-Si 500 g./t. (1.10 lb./t.)
Furnace deoxidation: Si-Mn 3900 g./t. (8.60 lb./t.)
Tapping temperature: 1600° C. (2912° F.)
Ingot weight: 14,400 kg.

During the pouring of molten steel from the ladle into the molds, ⅓ kg./t. (0.730 lb./t.), 1 kg./t. (2.20 lb./t.), and 1.5 kg./t. (3.30 lb./t.) of Fe-Cb was added to Molds Nos. 4, 5 and 6, respectively. The addition time and the particle size of Fe-Cb and the conditions of the subsequent hot rolling operation were the same as in the case of the inventive steel. No Fe-Cb was added to Mold No. 3, which was used as a comparative or control steel.

The chemical composition and mechanical properties are shown in Table 2.

TABLE 2

Mold No.	Fe-Cb addition, (kg./t.)	Chemical composition (percent) C	Si	Mn	Cb	Sol. Al
3	0	0.15	0.06	0.50	----------	None
4	⅔	0.16	0.06	0.51	0.010	None
5	1	0.15	0.07	0.49	0.035	None
6	1½	0.15	0.07	0.50	0.049	None

TENSION TEST RESULTS

Mold No.	Fe-Cb addition, (kg./t.)	T.S., kg./mm.² (p.s.i.)	Y/P., kg./mm.² (p.s.i.)	Elongation, percent	Impact value, kg./m. (ft.-lb.)
3	0	42.9 (61,000)	30.1 (42,800)	40.2	2.6 (18.8)
4	⅓	47.0 (66,900)	37.1 (52,800)	33.5	2.3 (16.6)
5	1	52.1 (74,100)	43.0 (61,200)	30.0	1.8 (13.0)
6	1½	58.6 (83,400)	47.7 (67,800)	27.5	1.4 (10.1)

As apparent from the results shown in Table 1 and Table 2, there is no substantial difference in strength and elongation between the inventive steel, prepared by adding columbium to semi-killed steel deoxidized solely by aluminum, and the conventional steel prepared by adding columbium to silicon deoxidized semi-killed steel. However, there is a distinct significant difference in impact value, and the steels produced according to the present invention have excellent toughness in the direction at right angle to the rolling direction. The inventive steel and the conventional steel were examined under a microscope and measured as the number of inclusions of more than 100μ length in 60 fields. The results are shown in Table 3.

TABLE 3

Type of steel	Mold No.	Number of inclusions of more than 100μ length in 60 fields Top	Middle	Bottom
Inventive steel	5	0	0	0
Conventional steel	5	19	14	15

As seen from the results in Table 3, in the inventive steel, large manganese silicate inclusions which cause hook cracks and bending cracks were reduced almost to nil.

From the steels of Table 3, bending test specimens of 100 mm. width and 200 mm. length (3.94 inches x 7.88 inches) were taken in the right angle direction to the rolling direction, and their critical bend radius was determined with various bending radii. The inventive steel could be bent 180° with a bend radius of 1.0 x plate thickness, whereas the conventional steel could be bent 180° only with a bend radius of 1.5 x plate thickness. FIG. 5 is a photograph showing the inclusions in these two specimens. The inclusions shown in FIG. 5(I) are of manganese silicates present in the conventional steel plate (Mold No. 5) which was produced by adding columbium to silicon deoxidized semi-killed steel. The inclusions shown in FIG. 5(II) are of the alumina of a size less than 100μ in the inventive steel (Mold No. 5) which was produced by adding columbium to semi-killed steel deoxidized by aluminum alone. The difference between these two types of inclusions causes the difference in the impact value for the steels in the right angle direction to the rolling direction and the bending quality.

EXAMPLE 2

A heat having the following ladle analysis was prepared (percent): C, 0.27; Mn, 1.00; Si, 0.01; P, 0.01; S, 0.016.

Ingots were made from this composition under the following conditions:

Amount of Al for ladle deoxidation: 205 g./t. (0.452 lb./t.)
Amount of Al for mold deoxidation:
Mold No. 3 100 g./t. (0.220 lb./t.)
Mold No. 4 97 g./t. (0.0215 lb./t.)
Mold No. 5 97 g./t. (0.215 lb./t.)
Tapping temperature: 1605° C. (2920° F.)
Ingot weight: 14,400 kg.

Fe-Cb was added to Mold Nos. 4 and 5 in an amount of ½ kg./t. (1.10 lb./t.) and 1 kg./t. (2.20 lb./t.), respectively. These ingots were hot rolled into plates of 6.0 mm. thickness (0.236 inch) under similar conditions as in Example 1. The chemical composition and mechanical properties of these plates are shown in Table 4.

TABLE 4

Mold No.	Fe-Cb addition, (kg./t.)	Chemical composition (percent) C	Si	Mn	Cb	Sol. Al
3	0	0.26	0.01	1.01	----------	0.013
4	½	0.27	0.01	1.02	0.017	0.011
5	1	0.27	0.01	1.01	0.032	0.011

TENSION TEST RESULTS

Mold No.	Fe-Cb addition, (kg./t.)	T.S., kg./mm.² (p.s.i.)	Y/P., kg./mm.² (p.s.i.)	Elongation, percent	Impact value, kg./m. (ft.-lb.)
3	0	53.6 (76,200)	38.0 (54,000)	32.5	3.5 (25.3)
4	½	56.4 (80,200)	45.7 (65,000)	27.4	2.9 (20.9)
5	1	61.3 (87,100)	49.7 (70,700)	26.5	2.6 (18.8)

The ingot making conditions for steel (convertor steel) according to the conventional method are as follows:

Ladle analysis (percent): C, 0.26; Si, 0.06; Mn, 0.98; P, 0.012; S, 0.017.
Ladle deoxidation: Fe-Si: 700 g./t. (1.54 lb./t.)
Tapping temperature: 1610° C. (2930° F.)
Ingot weight: 14,400 kg.

During the pouring into molds, Fe-Cb was added to Molds Nos. 4 and 5 in an amount of ½ kg./t. (1.10 lb./t.) and 1 kg./t. (2.20 lb./t.), respectively. These ingots were hot rolled to a thickness of 6.0 mm. (0.236 inch) under similar conditions as in the case of the inventive steel. Chemical analysis and mechanical properties of these plates are tabulated in Table 5.

TABLE 5

Mold No.	Fe-Cb addition, (kg./t.)	Chemical composition (percent) C	Si	Mn	Cb	Sol. Al
3	0	0.27	0.08	0.97	----------	None
4	½	0.27	0.07	0.98	0.019	None
5	1	0.28	0.07	0.98	0.031	None

TENSION TEST RESULTS

Mold No.	Fe-Cb addition, (kg./t.)	T.S., kg./mm.² (p.s.i.)	Y/P., kg./mm.² (p.s.i.)	Elongation, percent	Impact value, kg./m. (ft.-lb.)
3	0	53.4 (76,000)	40.2 (57,200)	30.5	2.3 (16.6)
4	½	56.5 (80,400)	43.1 (61,300)	27.0	1.6 (11.4)
5	1	61.9 (88,000)	49.5 (70,400)	26.1	1.3 (9.4)

As seen from the results of Tables 4 and 5, the inventive steel is excellent in respect to toughness in the right angle direction of the rolling direction. The steel produced according to the present invention and the steel produced according to the conventional method were inspected under a microscope to determine the number of inclusions of a length of more than 100μ. The results are shown in Table 6.

TABLE 6

Type of steel	Mold No.	Number of inclusions of more than 100μ length in 60 fields Top	Middle	Bottom
Inventive steel	4	0	0	0
Conventional steel	4	16	10	8

As in the steel of Example 1, the inventive steel was devoid of large size manganese silicate inclusions.

EXAMPLE 3

A high tensile strength steel plate containing columbian and produced according to the present invention and similar steel produced according to the conventional method were delivered to a steel pipe manufacturer. The ingot making conditions and rolling conditions for the steels are shown below. Fe-Cb was added to the ladle.

TABLE 7

Type of steel	Ladle analysis (percent) C	Si	Mn	P	S	Cb
Inventive steel	0.22	0.01	0.94	0.021	0.023	0.026
Conventional steel	0.21	0.06	0.94	0.015	0.013	0.024

TABLE 8

Type of steel	Addition of deoxidation agent Furnace addition	Ladle addition	Mold addition
Inventive steel		Al, 300 g./t. (0.660 lb./t.).	Al, 61 g./t. (0.134 lb./t.).
Conventional steel		Fe-Si, 1,000 g./t. (2.20 lb./t.).	

TABLE 9

Type of steel	Hot rolling temperature,° C. (°F). Heating temperature	Final finishing temperature	Coiling temperature
Inventive steel	1,280 (2,340)	850–865 (1,560–1,590)	600 (1,110)
Conventional steel	1,280 (2,340)	845–865 (1,550–1,590)	610 (1,130)

Both steels were rolled into coil form of 6.0 mm. (0.236 inch) thickness and 1214 mm. (4 feet) width. Table

10 shows the chemical composition of these plates. (Mold No. 3 was regarded as representative.)

TABLE 10

Type of steel	Portion	Chemical composition (percent) C	Si	Mn	P	S	Cb	Sol. Al
Inventive steel.	T	0.19	0.007	0.97	0.013	0.014	0.023	0.007
	M	0.21	0.009	0.97	0.015	0.015	0.022	0.008
	B	0.19	0.007	0.96	0.014	0.014	0.020	0.007
Conventional steel.	T	0.20	0.074	1.01	0.008	0.014	0.024	None
	M	0.22	0.080	1.04	0.012	0.016	0.022	None
	B	0.19	0.080	1.02	0.009	0.014	0.020	None

NOTE.—T=Top portion of ingot; M=middle portion of ingot; B=Bottom portion of ingot.

Table 11 indicates the mechanical properties of the steel plates of Table 10.

TABLE 11

Type of steel	Portion	Tensile strength, kg./mm.² (p.s.i.) L	C	Yield point, kg./mm.² (p.s.i.) L	C	Elongation (percent) L	C	Impact value, kg./m. (ft./lb.) L	C
Inventive steel	T	58.5 (83,200)	58.0 (82,500)	43.8 (62,300)	43.9 (62,400)	29.7	23.1	5.2 (37.5)	2.8 (20.2)
	M	58.8 (83,600)	59.0 (84,000)	44.5 (63,400)	45.1 (64,100)	29.5	23.7	5.6 (40.4)	2.9 (20.9)
	B	57.2 (81,400)	57.8 (82,200)	43.5 (61,900)	44.2 (62,800)	29.9	27.4	5.0 (36.1)	2.7 (19.5)
Conventional steel	T	59.9 (85,200)	60.4 (95,900)	44.8 (63,700)	45.0 (64,000)	27.8	23.0	5.0 (36.1)	1.6 (11.5)
	M	60.1 (85,500)	61.3 (87,200)	45.9 (65,300)	47.8 (68,000)	27.8	22.7	6.0 (43.3)	1.8 (13.0)
	B	58.3 (82,900)	59.0 (84,000)	45.1 (64,100)	45.0 (64,000)	28.1	25.6	4.9 (35.4)	1.5 (10.8)

NOTE.—L=Rolling direction; C=Right angle to rolling direction.

50 tons of each of these two types of steels were supplied to a steel pipe producer and processed into API pipe (X–52) of 16 inch diameter. The results are shown in Table 12.

TABLE 12

	Inventive steel	Conventional steel
Yield (percent)	88.69	41.10
Scrap (percent)	11.31	58.90
Breakdown (percent):		
Hook crack	1.00	50.00
Trimming loss	5.00	5.00
Open seam	2.00	1.30
Sampling loss	1.00	1.00
Others	2.31	1.60

The above results demonstrate a significant difference in the yield percentage between the two types of steel. This is due to the fact that the hook crack occurrence is only 1% in the steel produced according to the present invention while it is as high as 50% in the conventional steel of which 25 tons are defective. The hook cracks were sensed and detected by a supersonic detector positioned on the production line.

EXAMPLE 4

Mechanical tests were conducted on an inventive semi-killed steel plate containing columbium and/or vanadium and a conventional semi-killed steel plate containing columbium and/or vanadium. Table 13 shows the chemical composition of these steel plates, while Table 14 indicates their mechanical properties. Table 15 tabulates the results of microscopic measurement of the steel inclusions. No. 1 and No. 2 in each of the tables indicate conventional columbium-containing steels and No. 3 to No. 8 refer to the inventive steel plates. No. 3 and No. 4 are columbium-containing steels while No. 5 and No. 6 are vanadium-containing steels. No. 7 and No. 8 are steels containing both columbium and vanadium.

These steel plates were produced from different charges, but under production conditions as similar as possible. The hot rolling and mechanical testing conditions were similar to those of Example 1.

It should be noted that these steel plates have higher phosphorus, chrome and copper contents to increase their atmospheric resistance.

TABLE 13

No.	Chemical composition (percent) C	Si	Mn	P	S	Cu	Cr	Cb	V	Sol. Al
1	0.12	0.06	0.33	0.090	0.021	0.39	0.46	0.012	----------	None
2	0.11	0.07	0.34	0.089	0.019	0.39	0.46	0.054	----------	None
3	0.12	0.01	0.32	0.087	0.019	0.38	0.46	0.015	----------	0.006
4	0.12	0.01	0.30	0.089	0.022	0.38	0.46	0.056	----------	0.007
5	0.11	0.01	0.33	0.093	0.021	0.42	0.42	----------	0.032	0.006
6	0.12	0.01	0.34	0.092	0.024	0.43	0.43	----------	0.083	0.005
7	0.12	0.01	0.32	0.088	0.019	0.40	0.45	0.009	0.024	0.006
8	0.12	0.01	0.35	0.090	0.020	0.41	0.47	0.044	0.087	0.005

TABLE 14

Type of steel	No.	Tension test results T.S., kg./mm.² (p.s.i.)	Y.P., kg./mm.² (p.s.i.)	Elongation, percent	Impact value, kg./m. (ft.-lb.)
Conventional steel.	1	48.7 (69,300)	39.0 (55,400)	33.9	2.3 (16.6)
	2	55.5 (78,900)	45.5 (64,700)	28.7	1.7 (11.6)
Inventive steel.	3	48.6 (69,100)	38.2 (54,300)	35.1	3.5 (25.3)
	4	56.0 (79,600)	45.0 (64,000)	28.3	3.1 (22.4)
	5	47.2 (67,100)	36.8 (52,300)	36.2	3.7 (26.8)
	6	55.1 (78,400)	44.1 (62,700)	30.0	3.2 (23.2)
	7	49.3 (70,100)	38.2 (54,300)	34.5	3.5 (25.3)
	8	57.2 (81,300)	45.7 (65,000)	28.6	3.0 (21.7)

TABLE 15

Type of steel	No.	Number of inclusions of more than 100μ length Top	Middle	Bottom
Conventional steel	1	16	10	8
	2	17	11	12
Inventive steel	3	0	0	0
	4	0	0	0
	5	0	0	0
	6	0	0	0
	7	0	0	0
	8	0	0	0

As clearly seen from the results in Table 14, there is no substantial difference in strength and elongation between the inventive steels, obtained by adding vanadium and/or columbium to semi-killed steel deoxidized by aluminum alone, and the conventional steels obtained by adding columbium to semi-killed steel deoxidized by silicon. However, there is a distinctive difference in the results of the impact tests. The steels produced according to the present invention show excellent toughness, particularly in the C direction.

Table 15 also demonstrates that in the inventive steels, large manganese-silicate above 100μ inclusions are reduced to zero.

EXAMPLE 5

Mechanical tests were conducted on conventional semi-killed steels containing vanadium, and semi-killed steels containing both vanadium and columbium according to the present invention.

Table 16 shows the chemical composition of the steel samples while Table 17 indicates their mechanical properties. Table 18 tabulates the results of measurements of inclusions larger than 100μ.

No. 1 and No. 2 are conventional vanadium-containing steels, No. 3 through No. 6 refer to inventive steels. No. 3 and No. 4 are vanadium containing steels. No. 5 and No. 6 are steels containing both vanadium and columbium.

These steels were produced and tested under the same conditions.

TABLE 16

Type of steel	No.	Chemical composition (percent) C	Si	Mn	P	S	Cb	V	Sol. Al
Conventional steel	1	0.27	0.08	0.46	0.016	0.013	----------	0.030	None
	2	0.26	0.09	0.46	0.015	0.014	----------	0.152	None
Inventive steel	3	0.26	0.01	0.49	0.015	0.014	----------	0.033	0.005
	4	0.27	0.01	0.48	0.017	0.016	----------	0.160	0.006
	5	0.28	0.01	0.49	0.014	0.015	0.010	0.022	0.006
	6	0.26	0.01	0.49	0.015	0.014	0.038	0.065	0.005

TABLE 17

[Tensile strength testing results]

Type of steel	No.	T.S., kg./mm.² (p.s.i.)	Y.P., kg./mm.² (p.s.i.)	Elongation, percent	Impact strength, kg./m. (ft.-lb.)
Conventional steel	1	49.6 (70,500)	38.6 (54,900)	35.2	2.5 (17.1)
	2	57.5 (81,700)	43.7 (62,100)	30.1	1.7 (12.3)
Inventive steel	3	48.9 (69,500)	38.4 (54,600)	35.5	3.6 (26.1)
	4	57.7 (82,000)	44.4 (63,100)	28.9	3.1 (22.4)
	5	51.5 (73,200)	40.6 (57,700)	33.6	3.3 (23.9)
	6	57.8 (82,200)	45.8 (65,100)	29.4	2.7 (19.5)

TABLE 18

Type of steel	No.	Number of inclusions of more than 100μ length in 60 fields Top	Middle	Bottom
Conventional steel	1	16	8	9
	2	20	9	4
Inventive steel	3	0	0	0
	4	0	0	0
	5	0	0	0
	6	0	0	0

As is apparent from the above tables, particularly from the results of the mechanical tests, the inventive steels exhibit better impact strength than the conventional steel. This is due to the fact that the large managanese-siliacte inclusions were eliminated by the present method according to which semi-killed steel is produced by aluminum deoxidation. This fact is clearly demonstrated by Table 18 which indicates the absence of large inclusions over 100μ in the inventive steels.

EXAMPLE 6

Semi-killed high tensile strength steel plates produced according to the present method and semi-killed high tensile strength steel plates produced according to the conventional method were shipped to a steel pipe manufacturer for further processing.

Table 19 shows the chemical composition, Table 20 indicates the mechanical properties, and Table 21 tabulates the pipe production yields of the steel samples. In these tables, No. 1 is a conventional vanadium-containing steel, No. 2 is a vanadium-containing steel of the present invention, and No. 3 is an inventive steel containing columbium and vanadium.

These steels were produced under producing conditions as similar as possible.

TABLE 19

Type of steel	No.	Portion	Chemical composition (percent) C	Si	Mn	P	S	Cb	V	Sol. Al
Conventional steel	1	Top	0.20	0.07	0.63	0.022	0.022	----------	0.055	None
		Middle	.21	.08	.63	0.022	.022	----------	.057	None
		Bottom	.19	.07	.60	.018	.020	----------	.056	None
Inventive steel	2	Top	.20	.01	.65	.021	.019	----------	.060	.008
		Middle	.20	.01	.63	.019	.018	----------	.050	.08
		Bottom	.19	.01	.62	.018	.017	----------	.059	.06
	3	Top	.20	.01	.62	.013	.014	0.035	.064	.07
		Middle	.21	.01	.60	.012	.013	.035	.062	.08
		Bottom	.18	.01	.60	.012	.013	.033	.062	.06

TABLE 20

[Results of tension test]

Type of steel	No.	Portion	T.S., kg./mm.² (p.s.i.) L	T.S., kg./mm.² (p.s.i.) C	Y.P., kg./mm.² (p.s.i.) L	Y.P., kg./mm.² (p.s.i.) C	Elongation, percent L	Elongation, percent C	Impact value, kg./m. (ft.-lb.) L	Impact value, kg./m. (ft.-lb.) C
Conventional steel	1	Top	53.2 (75,600)	53.4 (75,900)	44.0 (62,500)	44.1 (62,700)	32.0	28.6	5.5 (39.8)	1.8 (13.0)
		Middle	54.6 (77,600)	55.0 (78,200)	44.2 (62,800)	44.8 (63,600)	33.2	29.0	5.4 (39.0)	1.5 (10.8)
		Bottom	54.0 (76,700)	54.6 (77,600)	45.1 (64,700)	45.0 (64,000)	33.1	29.0	5.4 (39.0)	1.7 (12.3)
Inventive steel	2	Top	54.6 (77,600)	54.6 (77,600)	43.3 (61,500)	44.0 (62,500)	32.6	27.8	5.8 (41.9)	3.2 (23.1)
		Middle	55.0 (78,200)	55.7 (79,100)	44.6 (66,400)	45.2 (64,200)	31.4	27.1	5.6 (40.5)	3.0 (21.7)
		Bottom	54.9 (78,000)	55.0 (78,200)	44.8 (63,600)	46.0 (65,400)	32.0	27.9	5.7 (41.2)	2.9 (21.0)
	3	Top	54.2 (77,000)	54.7 (77,800)	44.8 (63,600)	45.4 (64,500)	33.4	29.7	5.8 (41.9)	3.5 (25.3)
		Middle	54.8 (77,900)	55.5 (78,900)	45.6 (64,800)	45.8 (65,100)	33.2	27.9	5.9 (42.7)	3.4 (24.6)
		Bottom	54.8 (77,900)	55.3 (78,600)	45.6 (64,800)	45.9 (65,300)	33.6	28.3	5.5 (39.8)	3.4 (24.6)

TABLE 21

[Results of pipe production]

	Conventional steel (1)	Inventive steel (2)	Inventive steel (3)
Yield (percent)	45.23	85.32	88.20
Scrap (percent)	54.77	14.68	11.80
Breakdown (percent):			
Hook crack	42.50	1.60	1.20
Trimming loss	6.20	6.20	5.00
Open seam	3.00	3.00	2.30
Sampling loss	1.00	1.00	1.00
Others	2.07	2.88	2.30

As clearly shown in Table 20, the mechanical properties in C direction of both of the present steels are better than those of the conventional steel.

There is a substantial difference in the results of pipe production between the present steels and the conventional steel: in the conventional vanadium-containing steel the hook crack occurrence is 42.5%, whereas in the inventive steels it is reduced to 1.6% and 1.2%, respectively.

These hook cracks were detected by a supersonic wave detector placed on the production line.

It will thus be clearly understood that the inventive semi-killed high tensile strength steel plates have excellent properties.

While specific embodiments of the invention have been shown and described in detail to illustrate the application of the inventive principles, it will be understood that the invention may be embodied otherwise without departing from such principles.

What is claimed is:

1. In a semi-killed high tensile strength steel consisting essentially of between about 0.06 to 0.30% of carbon, between about 0.30 to 1.5% of manganese, not more than 0.02% of silicon, not more than 0.02% of acid soluble aluminum, and at least one of the elements columbium and vanadium in the ranges

Cb: about between 0.005 to 0.1% and

V: about between 0.02 to 0.40%

with the balance being essentially iron, the improvement which comprises that the steel is deoxidized by aluminum alone, that the alumina inclusions formed by the aluminum deoxidation are not larger than 100μ and that the steel is devoid of manganese silicate inclusions larger than 100μ.

2. The improvement as claimed in claim **1**, wherein the steel consist additionally of at least one of the elements copper, phosphorus and chromium in the following amounts:

Cu: not more than 0.5%;

P: not more than 0.10%; and

Cr: not more than 1.0%.

3. A steel plate made from the steel composition of claim **1** and substantially devoid of manganese silicate inclusions near its surface.

4. A steel plate as claimed in claim **3**, additionally consisting of at least one of the elements copper, phosphorus and chromium in the following amounts:

Cu: not more than 0.5%;

P: not more than 0.10%; and

Cr: not more than 1.0%.

5. In a method of producing high tensile strength semi-killed steel consisting essentially of

between about 0.06–0.30% of carbon,

between about 0.30–1.5% of manganese,

not more than 0.02% of silicon,

not more than 0.02% of acid soluble aluminum,

and at least one of the elements columbium and vanadium in the ranges

Cb: about between 0.005–0.1% and

V: about between 0.02–0.4%, with the balance being essentially iron,

the improvement which comprises deoxidizing said steel to its semi-killed state solely with aluminum, whereby the formation of manganese silicate inclusions larger than 100μ is essentially avoided and the alumina inclusions formed by the aluminum deoxidation are not larger than about 100μ.

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