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# (54) EXCELLENT-STRENGTH AND EXCELLENT-TOUGHNESS STEEL AND THE METHOD OF MANUFACTURING THE SAME

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(57)**ABSTRACT** 

A steel with excellent-strength and excellent-toughness comprises, by weight percent, C: 0.02 to less than 0.15%; Si: not greater than 1%; Mn: 0.3 to 2.5%; P: not greater than 0.05%; S: less than 0.004%; sol. Al: 0.001 to 0.1%; Ti: not greater than 0.02%; N: not greater than 0.009%; wherein, the metal structure of the steel contains either or both of martensite and bainite, or the tempered structure thereof; an aspect ratio of prior austenite grains is not greater than 1.5, the average short diameter of the prior austenite grains is within a range of 60 to 700 μm; and the contents of Ti, N, S and the short diameter dr of the prior austenite grains satisfy the following expression (1) and (2):

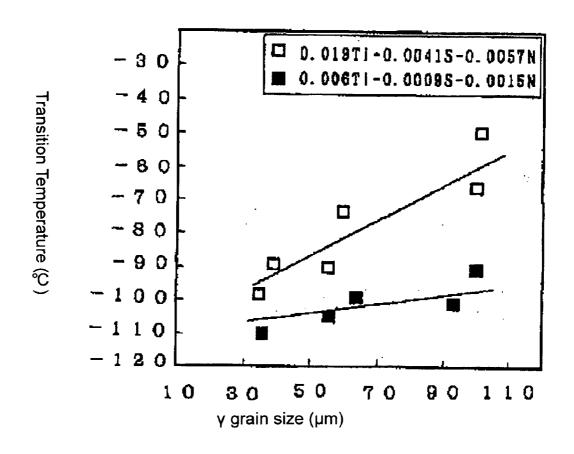
when Ti/N<3.4,

$$Ti + 8.1S \le \frac{0.315}{\sqrt{d\gamma - 30}} - 0.011$$
 (1)

when  $Ti/N \ge 3.4$ ,

$$3.4N + 8.1S \le \frac{0.315}{\sqrt{d\gamma - 30}} - 0.011 \tag{2}$$

The high-strength and excellent-toughness steel can be obtained with less alloy elements addition and produced with continuously high productivity.



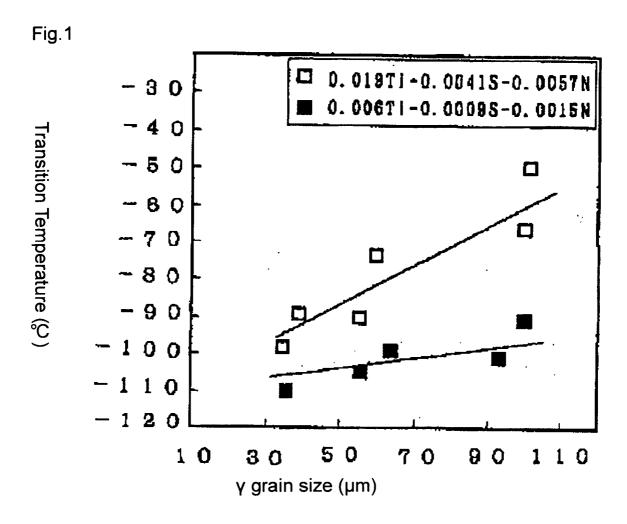
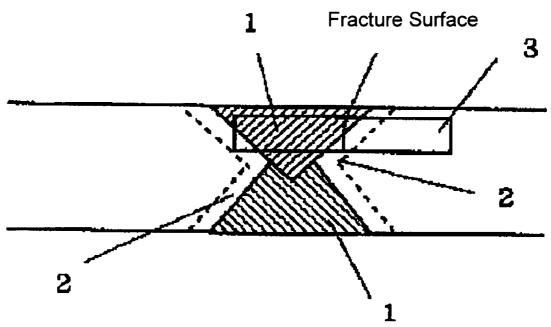


Fig.2



# EXCELLENT-STRENGTH AND EXCELLENT-TOUGHNESS STEEL AND THE METHOD OF MANUFACTURING THE SAME

#### TECHNICAL FIELD

[0001] The present invention relates to an excellent-strength and excellent-toughness steel and the method of manufacturing the same.

#### BACKGROUND ART

[0002] Steels, especial steel for structure, are usually required to have both excellent strength and excellent toughness. In order to meet this requirement without adding expensive elements such as Ni, a number of methods in respect of grain refinement of structures by thermal refining and rolling control have been proposed and employed hitherto.

[0003] For example, Japanese Patent Application Laid-Open No. S55-30050 dicloses a method of manufacturing a high-toughness steel, in which, chemical compositions, slab casting conditions and slab heating conditions during hot rolling are defined to make AlN finely disperse in steel, and thereby suppressing the growth of austenite grains, thus obtaining fine structure.

[0004] Although this method can fine crystal structure, it is obviously difficult to be employed in continuous casting with high efficiency since AlN is the precipitation which causes the lateral cracking of slab during the continuous casting. Japanese Patent Application Laid-Open No. S57-131320 discloses a method of manufacturing high-strength steel plate with excellent toughness at low temperature. In this method, the temperature at the end of rolling and the subsequent cooling rate are defined. However, the rolling efficiency of this method is quite low since the rolling at the temperature from austenite non-crystal area till the twophase area is required. Furthermore, although the fracture appearance transition temperature is ameliorated, separation is readily generated, and thus the absorption energy remarkably tends to be smaller. Therefore, when the absorptive energy is required to be or greater than a certain value of Charpy impact value, this method would not be effective.

[0005] Furthermore, Japanese Patent Application Laid-Open No. H7-258730 and No. H7-258731 have published a method of manufacturing a thick steel plate for structures, which has excellent-toughness and low sonic anisotropy. According to these methods, for decreasing the sonic anisotropy and ensuring the toughness, the grain refinement by re-crystallization of austenite is fully employed as possible, and meanwhile rolling is carried out to the areas not being re-crystallized.

[0006] Although this method does not utilize the rolling control effect, in order to obtain practically satisfied toughness, the temperature at the end of rolling must controlled at around 900° C. or lower, and therefore the problem of inefficient productivity caused by rolling at low temperature is unavoidable.

[0007] According to these methods, required toughness may be obtained by the skillful combination of heat treatment, cooling and reheating. But, productivity of any one of these methods is low in mass production.

#### DISCLOSURE OF THE INVENTION

[0008] The present invention is to provide steel with excellent-strength and excellent-toughness and a method of manufacturing the same. The manufacturing method can refine structure, in which the grain refinement of the structure by rolling control or the like that cause the decline of productivity is not necessary.

[0009] The excellent-strength and excellent-toughness steel and the method of manufacturing the same according to the present invention are described in details as follows.

[0010] 1) An excellent-strength and excellent-toughness steel comprising, by weight percent, C: 0.02 to less than 0.15%; Si: not greater than 1%; Mn: 0.3 to 2.5%; P: not greater than 0.05%; S: less than 0.004%; sol. Al: 0.001 to 0.1%; Ti: not greater than 0.02%; N: not greater than 0.009%; wherein its metal structure contains either or both of martensite and bainite, or the tempered structure thereof; an aspect ratio of prior austenite grains is not greater than 1.5, the average short diameter of the prior austenite grains is within a range of 60 to 700  $\mu$ m; and the contents of Ti, N, S and the short diameter dr of the prior austenite grains satisfy the following expression (1) and (2):

when Ti/N<3.4,

$$Ti + 8.1S \le \frac{0.315}{\sqrt{d\gamma - 30}} - 0.011$$
 (1)

when Ti/N≥3.4,

$$3.4N + 8.1S \le \frac{0.315}{\sqrt{d\gamma - 30}} - 0.011 \tag{2}$$

in which each symbol of element represents the content by weight percent of its corresponding element, and the unit of dr is  $\mu m$ .

[0011] 2) An excellent-strength and excellent-toughness steel with large heat input for welding comprising, by weight percent, C: 0.02 to less than 0.15%; Si: not greater than 1%; Mn: 0.3 to 2.5%; P: not greater than 0.05%; S: less than 0.004%; sol. Al: 0.001 to 0.1%; Ti: 0.004 to 0.02%; N: 0.001 to 0.009%; Ti/N: 0.4 to 4, wherein its metal structure contains either or both of martensite and bainite, or the tempered structure thereof; the aspect ratio of the prior austenite grains is not greater than 1.5, the average short diameter of the prior austenite grains is within a range of 60 to 700  $\mu m$ ; the contents of Ti, N, S and the short diameter dr of prior austenite grains satisfy the following expression (3) and (4):

$$Ti + 8.1S \le \frac{0.315}{\sqrt{d\gamma - 30}} - 0.011$$
 (3)

$$3.4N + 8.1S \le \frac{0.315}{\sqrt{d\gamma - 30}} - 0.011 \tag{4}$$

in which each symbol of element represents the content by weight percent of its corresponding element, and the unit of dr is  $\mu m$ .

[0012] 3) A method of manufacturing an excellent-strength and excellent-toughness steel described in the above-stated 1) or 2), in which, hot processing subjected to the steel having the chemical composition defined in above-stated 1) or 2) is terminated at a temperature of 950° C. or higher so as to making the short diameter of the prior austenite grains be 60 to 700  $\mu m$ , and quenching process is carried out directly.

[0013] Here, the size of the austenite grains (hereinafter referred to as  $\gamma$  grain) refers to the size of prior  $\gamma$  grains in the metal structure of steel cooled after hot processing. The boundary of the prior  $\gamma$  grain easily appears in the steel containing bainite and martensite due to etching, and the grain size can also be identified and measured using an optical microscope. In addition, the steels may be of any shapes, for typical examples, steel plates, steel pipe and profiled bar.

[0014] In order to exploit an excellent-toughness steel with tensile strength pf 400 MPa or greater without requiring the refinement of structure in its manufacturing process and a method for manufacturing the same, the present inventor applied the compact rolling mill and heat treatment furnace in lab to carry out experiments under various conditions, and investigated the strength and toughness of the steel.

[0015] At the beginning of the investigation, one object was to improve the production efficiency, so that the premise of the investigation was not to apply the grain-refining method relying on rolling control that decreases the rolling efficiency or the grain-refining method using reheating and quenching which requires reheating processing after rolling. Another object was to increase the finish temperature of hot processing as high as possible for improving productivity. However, without employing rolling control, the  $\gamma$  grains would absolutely become coarse at the end of rolling if both the raw material heating temperature and finish rolling temperature are increased.

[0016] On the other hand, if rolling control is employed, even for the coarse  $\gamma$  grains, the final structure can be refined to improve the toughness. However, if the rolling control is not employed, the toughness is difficultly be ensured if the refinement of  $\gamma$  grains is insufficient. In order to refine the crystal grains, the rolling should be carried out at a low temperature of 900° C. or lower, thus the objects described above cannot be obtained.

[0017] In fact, when carrying out the rolling test under the condition without rolling control, in order to ensure the fracture appearance transition temperature in Charpy impact test be not greater than  $-50^{\circ}$  C., the  $\gamma$  grains should be refined to 40  $\mu$ m or lower. Therefore, the refinement to obtain grain size of 40  $\mu$ m or smaller was comparatively easily realized by performing heating at a temperature of 900° C. or lower when the rolling is terminated at 900° C. or lower; or the reheating was performed from  $\alpha$ -region to realize reverse modification and the grain growth was pinned by AlN and NbC. However, if the temperature exceeds 1000° C., since the pinning grains disappear due to solid dissolving, grains becomes coarse and causes remarkable deterioration of toughness.

[0018] As the results of repeated investigation for developing the steel having excellent strength and excellent toughness that can be produced without the refinement of  $\gamma$  grains, the inventor obtained the following findings.

[0019] (1) For the steel with coarsened prior  $\gamma$  grains, although the toughness is deteriorated, the transition temperature and absorptive energy can be significantly ameliorated by reducing S content in the state of coarse grains and thus suppressing the precipitation of MnS. However, when  $\gamma$  grains are fine grain, this effect cannot be expected.

[0020] (2) TiN contained in steel also has bad influence on the toughness of steel. The transition temperature can be ameliorated by decreasing N or Ti content so as to decrease the precipitation of TiN. However, when the  $\gamma$  grains are fine grains, the transition temperature cannot be ameliorated.

[0021] (3) As described in (1) and (2), toughness-improving effect along with the purification by decreasing the precipitation of MnS and TiN is almost unobtainable in the steel metal structure not containing bainite or martensite or their tempered structure.

[0022] (4) Elements such as Ca and rare earth metals (REM), that form inclusions, are preferably decreased due to their bad influence on transition temperature in coarse V grains. However, the bad influence from Ca and REM is less compared to that that caused by Mns and TiN. Therefore, the reduction of these elements is not as important as that of MnS and TiN.

[0023] (5) If the precipitation of MnS and TiN is reduced sufficiently, even if the  $\gamma$  grains size exceeds 60  $\mu m$ , the increase of transition temperature is slight. Furthermore, even if a part of the  $\gamma$  grains size exceeds 100  $\mu m$ , the increase of the transition temperature is slight too.

[0024] (6) In the condition for limiting the precipitation of MnS and TiN, the strength can be improved by increasing hardness through the coarseness of  $\gamma$  grains. Therefore, the  $\gamma$  grains size would rather exceed 60  $\mu m$  so as to obtain high-strength steel at low cost. Furthermore, since the rolling control is not needed, the  $\gamma$  grains can transform from complete re-crystal phase so as to realize uniform structure, and thus producing excellent product stably. As an approximate value at re-crystal state, the aspect ratio of  $\gamma$  grains is set at not great than 1.5 as the proper condition to produce steel

[0025] (7) When  $\gamma$  grains are coarsened, the MnS and TiN contents need to be decreased properly according to the short diameter dr of  $\gamma$  grains. The  $\gamma$ -grain sizes can be limited by the expressions described below and ensure the high toughness within a wide range. However, if the  $\gamma$ -grain size exceeds 700  $\mu$ m, the bad influence on toughness caused by the grain coarseness cannot be ignored.

[0026] The present invention was made on the basis of these investigations. According to the present invention the productivity can be improved since the rolling control is not necessary.

# DESCRIPTION OF DRAWING

[0027] FIG. 1 is a graph showing the relationship between  $\gamma$ -grain size and toughness.

[0028] FIG. 2 is a graph showing the sampling location of Charpy impact test piece.

#### BEST MODE OF THE INVENTION

[0029] The best modes of the present invention are described as following referring to the drawings attached hereto.

[0030] FIG. 1 shows the relation of y-grain size and toughness, specifically, the results of the investigation in respect to the fracture appearance transition temperature by Charpy impact test performed with the steel (symbol □) containing 0.019% of Ti, 0.0041% of S and 0.0057% of N, and the steel (symbol ■) containing 0.006% of Ti, 0.0009% of S and 0.0015% of N, which were hot rolled under various rolling temperature.

[0031] As shown in FIG. 1, no matter how much the contents of Ti, S and N are, the toughness would decline if crystal grains grow. However, if the contents of Ti, S and N are decrease (as represented by  $\blacksquare$  in FIG. 1), especially if the content of S is decreased, the toughness would be improved significantly. Furthermore, the ameliorating effect of toughness is significant when  $\gamma$  grains size is large.

[0032] The reasons for limiting the chemical composition of the steel according to the present invention is specified as follows (hereinafter, % refers to as weight %).

[0033] C is an indispensable element for ensuring strength. If the C content is less than 0.02%, the required strength cannot be ensured. On the other hand, if the C content exceeds 0.15%, the toughness of heat affected zone at welded joints and base metal would be impaired significantly. Therefore, the C content is defined within a range of 0.02 to 0.15%.

[0034] Si is added for deoxidizing and improving the toughness of steel plate. However, if the Si content exceeds 1%, the toughness would be impaired. Therefore, the upper limit of the Si content is 1%. Furthermore, the Si content can be as low as possible provided that it does not bring impediment to the deoxidization of steel.

[0035] Mn is an effective element for improving hardness and ensuring the strength. However, if the Mn content is less than 0.3%, the toughness and strength required cannot be obtained due to the insufficient hardness. On the other hand, if the Mn content exceeds 2.5%, the toughness of heat affected zones at welded joints and base metal would be impaired due to the increase of segregation and excessive hardness. Therefore, the Mn content is defined within a range of 0.3 to 2.5%.

[0036] P exists in steel as unavoidable impurity. If the P content exceeds 0.05%, the segregation on boundary of crystal grains would degrade toughness and induce cracking at high temperature in welding. Thus, the P content is controlled at not greater than 0.05%.

[0037] S combines with Mn, Ca or REM to form forms oxysulfide and exists in steel as inclusions. When the strength of steel is low or the structure contains sufficiently fine grains, these inclusions would not bring severe influence on toughness. However, if the inclusions are in the structure coarsened to a certain extent, the S content should be limited to satisfy the expressions described below. Even though the content satisfies the expressions, the bad influence on toughness cannot be avoided when the content is 0.004% or greater. The S content is further preferably controlled to be lower than 003%.

[0038] Al is an indispensable element for deoxidizing. If the Al content is less than 0.001%, the steel quality would be impaired due to the insufficient deoxidization. However, if Al content exceeds 0.1%, the toughness of base metal and heat affected zone at welded joints would be impaired. Therefore, the upper limit of Al content is 0.1%.

[0039] In general, Ti is contained in steel for fixing N contained in steel to ameliorate high-temperature ductibility. However, since TiN is the cause of the decrease of toughness, the addition of Ti is not desired if possible. The allowance range of its content from the view point of toughness is defined the expression described below. However, even though the Ti content satisfies the expression stated below, the impairment to toughness can hardly avoided when its content exceeds 0.02%.

[0040] Furthermore, the extra purification of the steel for great heat input welding would probably cause extra coarseness of  $\gamma$  grains and deteriorate the toughness. Therefore, the Ti content is preferably controlled at not less than 0.004%, and the ratio of Ti/N is controlled within a range of 0.4 to 4.0.

[0041] N is an impurity causing the decrease of high-temperature ductibility. Generally, such negative influence can be avoided in the form of TiN owing to the Ti addition. However, in the present invention, TiN itself is also the cause of deterioration of toughness, so that the formation of TiN should be suppressed by reducing the content of N or Ti.

[0042] In order to obtain excellent toughness, the range of N content should satisfy the expression described below. However, even though the expression is satisfied, the impairment of toughness caused by TiN or N unfixed and dissolving in steel cannot be ignored when the N content exceeds of 0.009%. Furthermore, when the N content is not greater than 0.001% and S content decreases to the extent that MnS almost does not exist, the growth of  $\gamma$  grains becomes easy. Therefore, a part of  $\gamma$  grains of heat affected zone in welding joint would probably coarsened by arc welding with large heat input around 100 KJ/cm.

[0043] Although the toughness of the steel according to the present invention is not easily impaired by the coarseness of  $\gamma$  grains, the hardness and size of crystal grains in the heat affected zone at welded joints with large heat input do not distribute evenly, so that the allowable upper limit of size of  $\gamma$  grains is determined at 300  $\mu$ m from the viewpoint of toughness. Therefore, TiN must be contained to suppress the growth of  $\gamma$  grains in welding with large heat input. N content may be 0.001% or greater, and Ti may be also contained.

[0044] On another aspect, as to the steels without the need of being welded and the steels only welded with low heat input not greater than 40 KJ/cm, the N content may be reduced as lower as possible according to the economic permission.

[0045] If required, the steel of the present invention can further contain the following elements in addition to those describe above for improving the hardness and strength.

[0046] Cr is an effective element for improving hardness. Although minimally required hardness is ensured by the indispensable elements described above, Cr can be added to the steel for thick-wall steel pipes to further ensure its

hardness. When the Cr content is 0.02% or greater, both the hardness and the effect of tempering softening impedance can be improved. Therefore, the Cr content is preferably controlled at not less than 0.02%. However, if the Cr content exceeds 1.5%, the impairment on the toughness of welded joint cannot be avoided. Therefore, the Cr content is controlled at not greater than 1.5%.

[0047] Mo can be preferably contained in the steel for thick-wall steel pipes to further improve the hardness and tempering softening impedance. If Mo content is less than 0.02%, such effects cannot be obtained. Therefore, Mo content is preferably controlled at not less than 0.02%. However, if Mo content exceeds 1%, the toughness of welded joint will be deteriorated significantly. Therefore, the upper limit of the Mo content is 1%.

[0048] B is especially effective for improving the hardness and strength of y-grain boundary. The B content is preferably controlled at not greater than 0.003%.

[0049] Nb is the indispensable element in steels produced by so-called rolling control. However, in the present invention, since the rolling control is almost not employed, Nb is not the indispensable element. But, Nb is effective for further improving strength. If the Nb content is in excess, the enhanced precipitation after rolling at high temperature of 1000° C. or higher would impair the toughness severely. Therefore, the Nb content should be controlled at not greater than 0.015%, and preferably not greater than 0.01%.

[0050] V can realize the effect of improving strength due to enhanced precipitation with little influence on toughness and effective improvement on strength. If the V content exceeds 0.01%, besides the tempering softening impedance, it can improve the hardness. The V content is preferably controlled at 0.01% or higher. If the V content exceeds 0.15%, the toughness would be impaired significantly. Therefore, the V content is controlled at not greater than 0.15%.

[0051] Cu is effective for improving strength and corrosion resistance. When high yield strength and high corrosion resistance is further required, Cu may be added. If Cu content is 0.05% or greater, the hardness can be improved in direct quenching. Therefore, the Cu content is preferably controlled at not less than 0.05%. However, when the addition of Cu exceeds 1.5%, the further improvement of performances is not in proportion to the increase of cost. Therefore, the Cu content is controlled at not greater than 1.5%.

[0052] Ni is effective for increasing the toughness of matrix of the steel in solid-dissolving state. Therefore, when more excellent toughness should be obtained stably, Ni may be added. If the Ni content is 0.05% or greater, the improvement of hardness can be obtained. Therefore, the Ni content is preferably controlled at not less than 0.05%. However, if the addition of Ni exceeds 4%, there cannot obtain the melioration of quality corresponding to the cost improvement. Therefore, the Ni content is controlled at not greater than 4%.

[0053] Ca reacts with S contained in steel to form sulfide. This sulfide is different form MnS as it maintains the spherical shape after rolling without extending along the rolling direction. Therefore, if the generation of welding-inducing cracking or hydrogen-induced cracking (HIC) that

starts from tips of extended impurities need to be suppressed, such sulfide can be contained. If the Ca content is 0.0002% or greater, the toughness of welded joint can be improved. Therefore, the Ca content is preferably controlled at not less than 0.0002%. However, if the Ca content exceeds 0.004%, the decrease of cleanness will degrade the toughness of base metal.

[0054] REM contributes to the refinement of the structure of heat affected zone at welded joints and the fixing of S while it would form inclusion to decrease the cleanness. However, since the impairment to toughness caused by the inclusion formed by addition of REM is slight, the decrease of toughness is allowable when REM content is determined not greater than 0.004%.

[0055] Next, the metal structure and prior austenite grains are described as follows.

## 1) Metal Structure

[0056] In order to obtain tensile strength of 450 MPa or higher, the metal structure of steel should comprise one or both of bainite and martensite generated by transformation at low temperature, or their tempered structure, and others containing ferrite and pearlite. Said structure can be obtained by hot rolling, then quenching from y-state, and tempering according to the requirement.

### 2) Aspect Ratio of Prior γ Grains

[0057] The reason for setting the average aspect ratio of prior  $\gamma$  grains at 1.5 or lower is to prevent the reduction of anisotropy and the decrease of strength. For the  $\gamma$  grains interiorly containing dislocation due to processing, the  $\alpha$  phase would also occur nucleation from the dislocation inside the grains, so that the hardness and toughness is degraded. In order to prevent such phenomena, the  $\gamma$  grains should be re-crystallized sufficiently (the aspect ratio approaching 1 with the progress of re-crystallization), then transformed. If the average aspect ratio of prior  $\gamma$  grains is 1.5 or lower, the decrease of strength can be prevented.

[0058] Furthermore, the average aspect ratio of prior  $\gamma$  grains is obtained by selecting a portion where the most extending side of  $\gamma$  grains can be observed, and cutting one test piece for the use of optical microscope and expressing its fibrous structure, then measuring the prior  $\gamma$  grains by image processing, and calculating the ratio of long diameter to short diameter as the average value of each  $\gamma$  grains in the form of an approximate oval.

# 3) Average Short Diameter of Prior γ Grains

[0059] In the present invention, since the processing at low temperature is not performed in order to improve productivity, the prior  $\gamma$  grains are comparatively coarse. Furthermore, due to the coarse grains, the reduction of Ti, N and S would bring significant effects to the toughness and strength. If the average short diameter of prior  $\gamma$  grains is less than 60  $\mu$ m, the strength and toughness required cannot be obtained. On the other hand, if the average short diameter of prior  $\gamma$  grains exceeds 700  $\mu$ m, the extra-coarseness would cause the deterioration of toughness.

4) Expression Showing the Relationship Between Ti, N, S and Short Diameter of Prior  $\gamma\mbox{ Grains}$ 

[0060] When the content ratio of Ti/N is less than 3.4, i.e. the N content is greater than that of Ti, if the expression (1)

below is not satisfied, the Ti and S contents are in excess, thus bringing the deterioration of toughness due to the excessive contents of TiN and MnS. This expression is concluded on the basis of several experiments. The proper content of Ti and S is determined according to the short diameter of prior  $\gamma$  grains.

[0061] When Ti/N<3.4,

$$Ti + 8.1S \le \frac{0.315}{\sqrt{d\gamma - 30}} - 0.011$$
 (1)

[0062] Furthermore, when the content ratio of Ti/N is not less than 3.4, i.e. the N content is less than that of Ti, if the expression (2) below is not satisfied, the Ti and S contents are in excess, thus bringing the deterioration of toughness due to the excessive contents of TiN and MnS.

[0063] When  $Ti/N \ge 3.4$ ,

$$3.4N + 8.1S \le \frac{0.315}{\sqrt{d\gamma - 30}} - 0.011$$
 (2)

[0064] When the steel of the present invention is used for welding with large heat input, the Ti/N is within a range of 0.4 to 4, and if expression (3) and (4) below are not satisfied, the extra-coarseness of  $\gamma$  grains in the heat affect zone at welded joint would cause the impairment of toughness of this portion. That is, when the welding with large heat input is carried out, the Ti and N contents required should be little greater so as to suppress the growth of grains in heat affected zone owing to the precipitation of TiN and MnS in some extent.

$$Ti + 8.1S \le \frac{0.315}{\sqrt{d\gamma - 30}} - 0.011$$
 (3)

$$3.4N + 8.1S \le \frac{0.315}{\sqrt{d\gamma - 30}} - 0.011 \tag{4}$$

[0065] In the above expression, each atomic symbol represents the content of its corresponding element by weight percent, and  $\mu m$  is the unit of dr.

[0066] Next, the manufacturing method of steel of the present steel is described in details.

[0067] When the steel with the chemical composition described above is subjected to hot processing, the austenite grains with short diameter of 60 to 700  $\mu$ m can be obtained at the end of thermal processing by controlling the processing temperature, and then the steel is direct quenched to obtain excellent strength and toughness.

[0068] The hot processing temperature to obtain austenite grains with short diameter of 60 to 700  $\mu m$  at the end of processing is defined depending on the chemical composition and processing extent. In general, it is set at 950° C. or higher as a reference value. Furthermore, if the size of prior  $\gamma$  grains is not great than 700  $\mu m$ , the excellent quality of steel can be obtained no matter how high the refinement temperature is. However, in practical producing lines, it is difficult to ensure the refinement temperature exceeding 1150° C. Furthermore, this temperature would increase the waste of steel due to the generation of scale. Therefore, the upper limit of the refinement temperature is defined to be around 1150° C.

[0069] Although there is no necessity to carry out hot rolling at low temperature for ensuring toughness, the hot rolling of 30% or higher at temperature area not greater than 900° C. would cause the generation of refinement of γ grains and rolling control effects, and thereby probably decreasing the strength greatly. Since in the steel production, this property would be the cause of the quality unevenness, the processing process at low temperature should be avoided. In order to avoid the bad influence, the ending temperature of hot rolling must be controlled so as to make the size of prior γ grains not less than 60 μm and make the γ grains be water-cooled under the state of not being hardened by processing. The cooling for quenching process after machining processing is not necessarily to be water cooling. However, since the martensite or bainite in the structures at least after transformation are desired to occupy 40% or more area in the micro structure, the cooling needs to be controlled for realizing this structure. Such cooling conditions can be estimated from CCT graph.

# **EXAMPLES**

[0070] Round steel ingots with sixteen kinds of chemical compositions shown in Table 1 were melted in a vacuum melting furnace. In addition, steels with ten kinds of chemical compositions shown in Table 2 were melted in a 250t converter to obtain slabs with thickness of 150 to 300 mm by continuous casting.

TABLE 1

	(The balance are Fe and unavoidable impurities)												
	Mark	С	Si	Mn	P	S	Al	Ti	N	Others	Ti/N		
Examples	1	0.096	0.30	1.35	0.009	34	0.021	0.005	14	B: 8, Ca: 2, Mg: 3	6.40		
•	2	0.137	0.19	1.26	0.009	12	0.023	0.006	14	Ca: 2, Mg: 4	4.11		
	3	0.036	0.16	2.21	0.011	16	0.023	0.017	40	Ca: 2, Mg: 2	4.25		
	4	0.061	0.19	1.43	0.010	12	0.026	0.004	6	Cr: 0.10, Mo: 0.29, Ca: 2, Mg: 3	7.02		
	5	0.095	0.18	0.91	0.012	7	0.028	0.006	10	Ni: 0.48, Cr: 0.15, Mo: 0.61, Ca: 2, Mg: 2	5.57		
	6	0.050	0.16	0.78	0.009	5	0.029	0.001	5	Ni: 0.19, 1Cr: 0.99, Mo: 0.14, Ca: 2, Mg: 3	1.82		
	7	0.049	0.32	1.07	0.011	5	0.025	0.002	22	Cu: 1.21, Ni: 0.78, Ca: 2, Mg: 4, REM: 6	3.17		
	8	0.052	0.10	1.34	0.010	8	0.024	0.008	20	NB: 0.010, V: 0.029, Ca: 2, Mg: 4	3.87		

TABLE 1-continued

	(The balance are Fe and unavoidable impurities)												
	Mark	С	Si	Mn	P	S	Al	Ti	N	Others	Ti/N		
Comparative	9	0.100	0.29	1.31	0.010	51*	0.026	0.009	33	B: 8, Ca: 2, Mg: 3	2.76		
Examples	10	0.138	0.20	1.26	0.010	58*	0.026	0.029*	30	Ca: 2, Mg: 3	9.56		
•	11	0.037	0.15	2.18	0.010	19	0.028	0.025*	69	Ca: 2, Mg: 41	3.68		
	12	0.061	0.19	1.38	0.010	8	0.027	0.002	98*	Cr: 0.10, Mo: 0.31, Ca: 2, Mg: 3	0.22		
	13*	0.099	0.20	0.92	0.011	19	0.026	0.004	11	Ni: 0.50, Cr: 0.15, Mo: 0.63, Ca: 2, Mg: 2	4.00		
	14	0.051	0.15	0.79	0.008	22	0.026	0.021*	45	Ni: 0.19, Cr: 1.05, Mo: 0.15, Ca: 48, Mg: 3	40.35		
	15*	0.051	0.30	1.08	0.010	9	0.027	0.011	32	Cu: 1.23, Ni: 0.78, Ca: 2, Mg: 4, REM: 43	3.37		
	16*	0.048	0.10	1.34	0.010	26	0.025	0.010	19	Nb: 0.022, V: 0.049, Ca: 2, Mg: 3	5.50		

(the unit of S, N, B, Ca, REM is ppm, others are weight %, \*represents the condition beyond the range prescribed in the present invention, Marks 13, 15 and 16 do not satisfy expression prescribed in the present invention (refer to Table 3))

[0071]

TABLE 2

	(The balance being Fe and unavoidable impurities)												
	Mark	С	Si	Mn	P	s	Al	Ti	N	Others	Ti/N		
Examples	17	0.072	0.32	1.49	0.011	12	0.027	0.011	40		2.75		
•	18	0.118	0.28	0.52	0.010	12	0.024	0.007	19		3.62		
	19	0.082	0.24	1.10	0.009	5	0.024	0.006	24	Cu: 0.31, Ni: 0.35	3.01		
	20	0.073	0.20	1.42	0.008	10	0.028	0.012	33	Cr: 0.10, Mo: 0.10, Nb: 0.06, Ca: 2, Mg: 3	3.69		
	21	0.048	0.11	1.31	0.010	14	0.028	0.007	23	V: 0.110, Ca: 2, Mg: 3, REM: 10	3.07		
Comparative	22	0.068	0.32	1.45	0.009	29	0.024	0.006	9		6.44		
Examples	23	0.124	0.28	0.50	0.008	8	0.028	0.010	100*		0.98		
	24	0.077	0.25	1.18	0.010	9	0.027	0.002**	6	Cu: 0.31, Ni: 0.34	3.05		
	25	0.071	0.19	1.38	0.011	8	0.024	0.002**	54	Cr: 0.10, Mo: 0.10, Nb: 0.004, Ca: 2, Mg: 3	0.36*		
	26	0.050	0.11	1.26	0.010	8	0.026	0.001**	9	V: 0.106, 2Mg: 2, REM: 49	3.05		

(The unit of S, N, B, Ca, REM is ppm, others are weight %, \*represents the condition beyond the range prescribed in the present invention. \*\*represents the condition beyond the range prescribed in the present invention when used as steel with large heat input.)

[0072] As shown in Table 3, the ingots were cast to obtain thick plates with thickness of 120 to 170 mm, and the thick plates were heated at temperature of 1180 to 1270° C., and then hot rolled to obtain hot-rolled steel plates with thickness of 25 to 50 mm.

[0073] Further, the continuously cast slabs were heated at temperature of 1200 to 1250° C. as shown in Table 4, and then hot rolled to obtain hot-rolled steel plates with thickness of 25 to 40 mm. These hot-rolled steel plates were subjected to water quenching, and a part of them were subjected to quenching-tempering under the condition shown in Table 3 and Table 4.

TABLE 3

	Mark	Short diameter of Prior y grains	Aspect ratio	Ti/N	Left Point of Expression 1	Right Point of Expression 1	Thickness of Raw Material (mm)	Heating temp. Of Raw Material (° C.)	Thickness of final product (mm)	Temp. at end of rolling (° C.)
Examples	1	62	1.1	6.40	0.032	0.045	300	1250	25	990
	2	72	1.2	4.11	0.015	0.037	200	1200	25	1080
	3	69	1.2	4.25	0.026	0.039	150	1270	40	1100
	4	61	1.0	7.02	0.012	0.045	300	1180	20	1000
	5	210	1.1	5.57	0.009	0.012	150	1250	35	1110
	6	67	1.2	1.82	0.005	0.041	150	1210	40	1070
	7	310	1.1	3.17	0.006	0.008	120	1270	50	1150
	8	57	1.5	3.87	0.013	0.049	200	1270	35	1070
Comparative	9*	59	1.2	2.76	0.050	0.047**	300	1250	25	990
Examples	10*	73	1.3	9.56	0.057	0.037**	200	1200	25	1090
•	11*	58	1.1	3.68	0.039	0.049	150	1270	40	1110
	12*	67	1.2	0.22	0.008	0.040	300	1180	20	990
	13	188	1.0	4.00	0.019	0.014**	150	1250	35	1110
	14*	77	1.3	40.35	0.033	0.035	150	1210	40	1070
	15	250	1.1	3.37	0.018	0.010**	120	1250	50	1140
	16	57*	1.4	5.50	0.015	0.028**	200	1270	35	1060

TABLE 3-continued

	Mark	Heat treatment	Tempering Temp. (° C.)	Yield Strength (MPa)	Tensile Strength (Mpa)	Transition Temp. vTrs (° C.)
Examples	1	Water quenching	600	473	563	-73
	2	Water cooling till 500° C.	_	437	534	-97
	3	Water quenching	600	485	570	-59
	4	Water quenching	600	530	608	-107
	5	Water cooling till 500° C.	_	506	586	-91
	6	Water cooling till 500° C.	_	501	581	-82
	7	Water quenching	600	477	560	-54
	8	Water quenching	600	518	595	-92
Comparative	9*	Water quenching	600	479	569	-45
Examples	10*	Water cooling till 500° C.	_	426	528	-26
	11*	Water quenching	600	481	574	-16
	12*	Water quenching	600	504	580	-20
	13	Water cooling till 500° C.	_	506	584	-18
	14*	Water cooling till 500° C.	_	499	580	-29
	15	Water quenching	600	475	568	22
	16	Water quenching	600	544	618	-10

<sup>(\*</sup>represents the conditions beyond the range prescribed in the present invention. In the mark column, \*represents the compositions beyond the range prescribed in present invention. \*\*represents the conditions not satisfying the expression prescribed in the present invention)

[0074]

TABLE 4

	Mark	Short diameter of Prior γ grains	Aspect ratio	Ti/N	Left Point of Expression 1	Right Point of Expression 1	Thickness of Raw Material (mm)	Heating temp. Of Raw Material (° C.)	Thickness of final product (mm)	Temp. at end o rolling (° C.)
Examples	17	80	1.0	2.75	0.021	0.034	300	1250	30	1090
	18	63	1.1	3.62	0.016	0.044	300	1200	25	1060
	19	144	1.2	3.01	0.010	0.018	200	1250	30	1150
	20	73	1.2	3.69	0.019	0.037	200	1230	40	1050
	21	53	1.2	3.07	0.018	0.055	150	1250	40	990
Comparative	22	87	1.2	6.44*	0.026	0.031	300	1250	30	1090
Examples	23*	39	1.1	0.98	0.016	0.095	300	1200	25	1060
-	24*	70	1.1	3.05	0.010	0.039	200	1250	30	1150
	25*	144	1.2	0.36*	0.009	0.018	200	1230	40	1050
	26*	51	1.2	3.05	0.007	0.057	150	1250	40	990

Mark	Heat treatment	Tempering Temp.	Yield Strength (MPa)	Tensile Strength (Mpa)	Transition Temp. (° C.)	Transition Temp. at joint (° C.)
Examples 17	Water quenching	600	410	518	-89	-64
18	Water cooling till 500° C.	_	398	511	-87	-50
19	Water quenching	600	415	520	-77	-56
20	Water quenching	600	427	527	-73	-50
21	Water quenching	600	465	559	-70	-44
Comparative 22	Water quenching	600	428	526	-99	-43
Examples 23*	Water cooling till 500° C.	_	397	510	-25	-39
24*	Water quenching	600	415	518	-126	-36
25*	Water quenching	600	428	523	-104	-34
26*	Water quenching	600	458	553	-51	-22

<sup>(\*</sup>represents the conditions beyond the range prescribed in the present invention. In the mark column, \*represents the compositions beyond the range prescribed in the present invention.)

[0075] JIS 4 Charpy test pieces and round bar tensile test piece were taken from each hot rolled steel plate after heat treatment to carry out the Charpy impact test and tensile test.

[0076] Further, the hot rolled steel plate marked as 17 to 26 was used to make welded joint by arc welding, and were subjected to the Charpy impact test. The welding was

two-surface-one-layer welding of a V-type notch and the heat input was 70 KJ/cm for the 30t or lower steel and 100 KJ/cm for the 30t or higher steel.

[0077] FIG. 2 shows the sampling location of Charpy impact test piece. As showed in the same figure, on the fracture surface of test piece 1 after test (notch portion), the

weld metal zone 1 and weld heat affected zone are substantially half and half.

[0078] Tables 3 and 4 show the test results. As shown clearly in Table 3, although the  $\gamma$  grains became coarse as the result of ending the hot rolling at high temperature of 990 to 1100° C., the examples of the present invention show the sufficient toughness for any use at the temperature of  $-50^\circ$  C. or lower.

[0079] Furthermore, since the Nb content in the composition of steel is small or substantially zero, although it is disadvantage for ensuring the strength, the yield strength of 400 to 500 MPa can be obtained due to the improvement of hardness owing to the coarseness of  $\gamma$  grains.

[0080] Table 4 shows the results of hot-cycle test and the mechanical characters of the base metal as well.

[0081] The examples marked as 17 to 21 show excellent toughness of heat affected zone at welded joints. Although the comparative examples marked as 22, 24 and 25 also showed the excellent toughness after being heat treated, the toughness of heat affected zone was impaired greatly for the extra-cleanness of steel.

[0082] The casting materials marked as 1 to 8 in Table 1 were hot rolled at low temperature of 900° C. or lower. The conditions of hot rolling and heat treatment were shown in Table 5. Each test described above was carried out to the steel plates after heat treatment. Their results were also shown in Table 5.

#### EFFECTS OF THE INVENTION

[0084] According to the present invention, high-strength and excellent-toughness steel can be obtained with less alloy elements addition and can be produced with continuously high productivity. Therefore, production amount of high-performance steel can be increased without upgrading equipment, and this is extremely advantageous in steel production.

1. An excellent-strength and excellent-toughness steel comprising, by weight percent, C: 0.02 to less than 0.15%; Si: not greater than 1%; Mn: 0.3 to 2.5%; P: not greater than 0.05%; S: less than 0.004%; sol. Al: 0.001 to 0.1%; Ti: not greater than 0.02%; N: not greater than 0.009%; wherein, the metal structure of the steel contains either or both of martensite and bainite, or the tempered structure thereof; an aspect ratio of prior austenite grains is not greater than 1.5, the average short diameter of the prior austenite grains is within a range of 60 to 700  $\mu m$ ; and the contents of Ti, N, S and the short diameter dr of the prior austenite grains satisfy the following expression (1) and (2): when Ti/N<3.4,

$$Ti + 8.1S \le \frac{0.315}{\sqrt{d\gamma - 30}} - 0.011 \tag{1}$$

TABLE 5

	Mark	Short diameter of Prior γ grains	Aspect ratio	Thickness of Raw Material (mm)	Heating temp. Of Raw Material (° C.)	Thickness of final product (mm)	Temp. at end of rolling (° C.)	Heat treatment	Tempering Temp. (° C.)	Yield Strength (MPa)	Tensile Strength (Mpa)	Transition Temp. vTrs (° C.)
Comparative	1	30*	2.2	300	1250	25	810	Water quenching	600	378	492	-92
Examples	2	28*	1.9	200	1200	25	830	Water cooling till 500° C.	_	337	478	-100
	3	27*	2.1	150	1270	40	780	Water quenching	600	382	498	-73
	4	31*	2.2	300	1180	20	800	Water quenching	600	435	533	-125
	5	36*	1.7	200	1200	35	840	Water cooling till 500° C.	_	409	517	-96
	6	32*	1.9	150	1210	40	830	Water cooling till 500° C.	_	399	511	-96
	7	35*	1.8	300	1250	50	850	Water quenching	600	377	493	-71
	8	35*	2.0	200	1270	35	880	Water quenching	600	445	542	-98

(\*represents the conditions beyond the range prescribed in the present invention.)

[0083] Although the refinement by rolling at low temperature can somewhat ameliorate the toughness, it can be known by comparing the results in table 5 to those in Table 3 that the strength was degraded significantly. Taking into consideration that the sufficient toughness has already been ensured at the stage of Table 3, the refinement by rolling at low temperature that merely impair the strength has no advantages. On the basis of the fact that the steel being re-heated at high temperature and quenched in Table 4 shows excellent strength and toughness, the steel shown in Table 5, for which the temperature was extra-lowered, may be re-heated in a heating furnace to  $1000^{\circ}$  C. or higher before water cooling, re-crystallized sufficiently, coarsening the  $\gamma$  grains, and then water-cooled so as to realize good performances

when Ti/N≥3.4,

$$3.4N + 8.1S \le \frac{0.315}{\sqrt{d\gamma - 30}} - 0.011 \tag{2}$$

in which each symbol of element represents the content by weight percent of its corresponding element, and the unit of dr is  $\mu m$ .

2. An excellent-strength and excellent-toughness steel with large heat input for welding comprising, by weight percent, C: 0.02 to less than 0.15%; Si: not greater than 1%; Mn: 0.3 to 2.5%; P: not greater than 0.05%; S: less than 0.004%; sol. Al: 0.001 to 0.1%; Ti: 0.004 to 0.02%; N: 0.001

to 0.009%; Ti/N: 0.4 to 4, wherein, the metal structure of the contains either or both of martensite and bainite, or the tempered structure thereof; the aspect ratio of the prior austenite grains is not greater than 1.5, the average short diameter of the prior austenite grains is within a range of 60 to 700  $\mu$ m; and the contents of Ti, N, S and the short diameter dr of prior austenite grains satisfy the following expression (3) and (4):

$$Ti + 8.1S \le \frac{0.315}{\sqrt{d\gamma - 30}} - 0.011 \tag{3}$$

$$3.4N + 8.1S \le \frac{0.315}{\sqrt{d\gamma - 30}} - 0.011 \tag{4}$$

in which each symbol of element represents the content by weight percent of its corresponding element, and the unit of dr is  $\mu m$ .

- 3. A method of manufacturing an excellent-strength and excellent-toughness steel, wherein, hot processing subjected to the steel having the chemical composition defined in claim 1 is terminated at a temperature of 950° C. or higher for making the short diameter of the prior austenite grains be 60 to 700  $\mu$ m, and quenching process is carried out directly.
- 4. A method of manufacturing an excellent-strength and excellent-toughness steel, wherein, hot processing subjected to the steel having the chemical composition defined in claim 2 is terminated at a temperature of 950° C. or higher for making the short diameter of the prior austenite grains be 60 to 700 µm, and quenching process is carried out directly.

\* \* \* \* \*