

[54] **METHOD FOR PRODUCING STEEL MATERIALS FOR LARGE HEAT-INPUT WELDING**

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[30] **Foreign Application Priority Data**

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[52] U.S. Cl. .... **148/12.3**

[51] Int. Cl.<sup>2</sup>..... **C21D 7/14**

[58] Field of Search..... 148/12.3, 142

[56]

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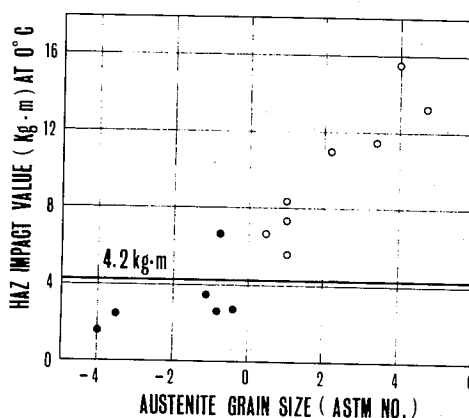
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[57]

**ABSTRACT**

A method for producing steel materials suitable for large heat-input welding which comprises heating a steel ingot or slab containing 0.03 to 0.18% C, 0.1 to 1.0% Si, 0.5 to 1.8% Mn, not more than 0.1% total Al, 0.004 to 0.03% Ti, 0.001 to 0.009% total N, with the balance being Fe and unavoidable impurities to a temperature between 1250° and 1400°C so as to dissolve into solid solution not less than 0.004% TiN, and then reprecipitating the dissolved TiN into fine TiN.

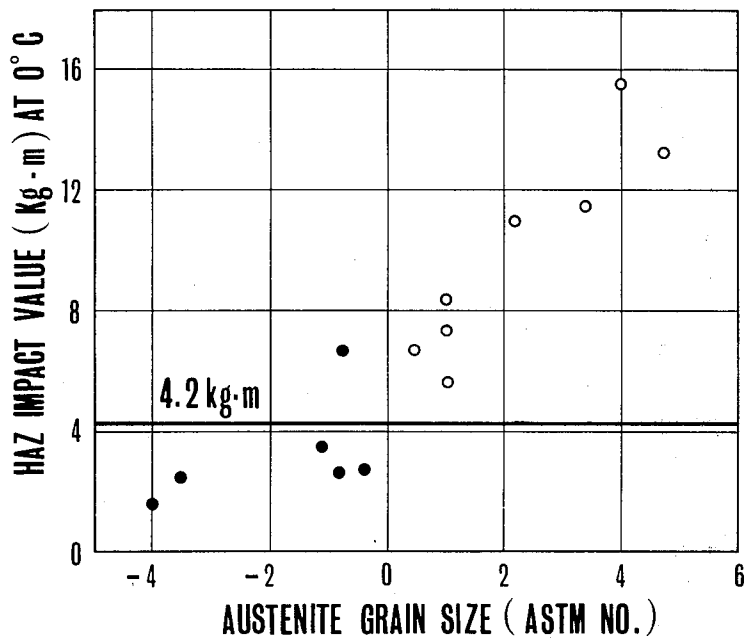
**16 Claims, 8 Drawing Figures**



• COMPARATIVE STEEL

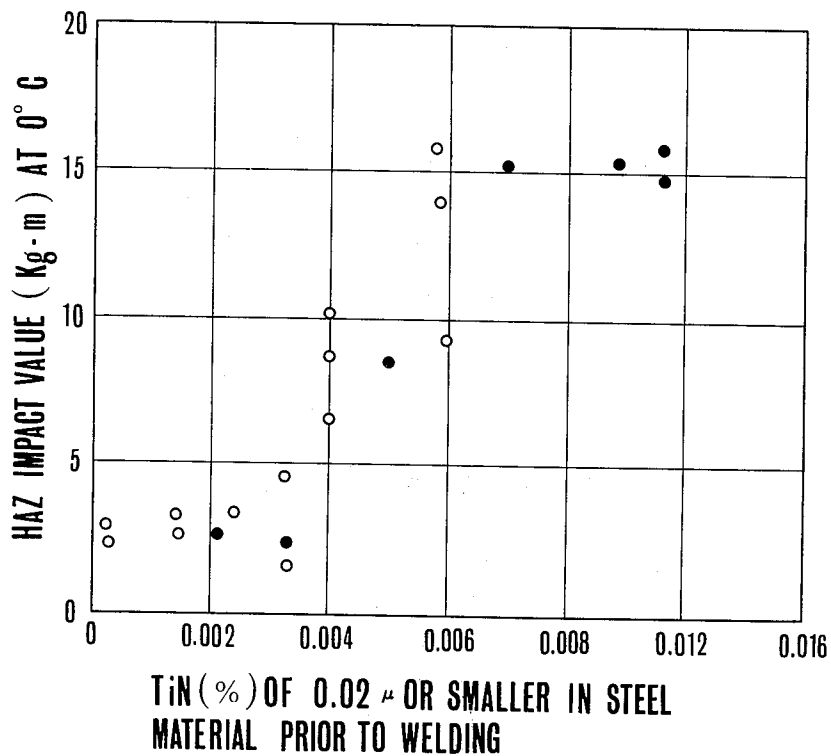
◦ STEEL ACCORDING TO THE PRESENT INVENTION

FIG. 1



• COMPARATIVE STEEL

○ STEEL ACCORDING TO THE PRESENT INVENTION

*FIG. 2*

○ STEEL (2) - 10

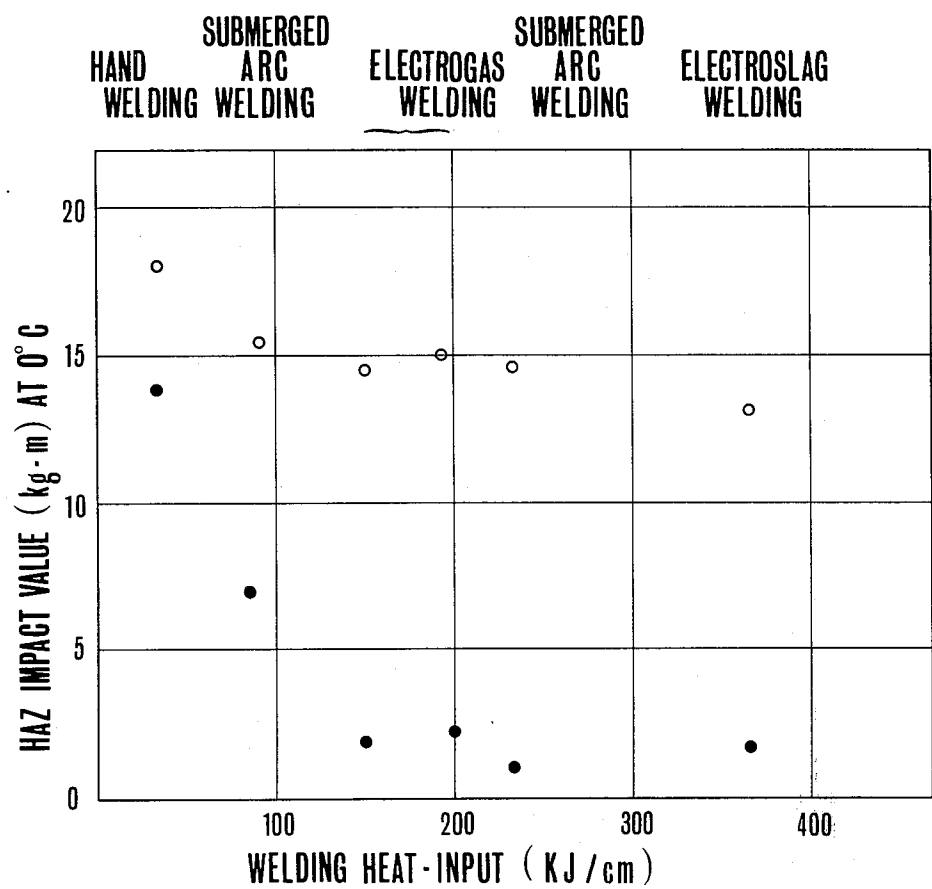
• STEEL (2) - 2

WELDING METHOD: ELECTROGAS WELDING

HEAT-INPUT: 190 KJ/cm

PLATE THICKNESS: 32mm (AS ROLLED)

FIG. 3



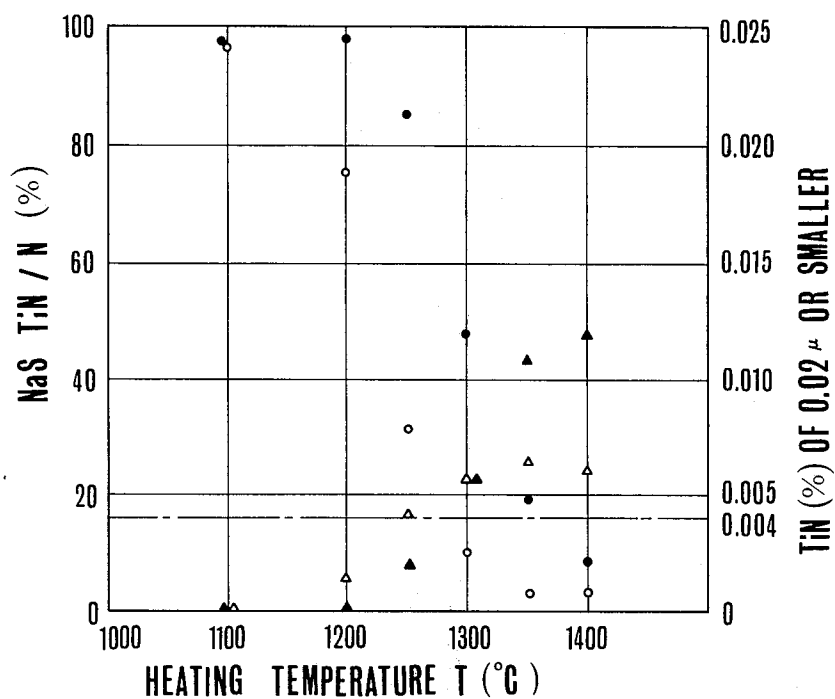
STEEL

○ (2) - 10

• (2) - 9

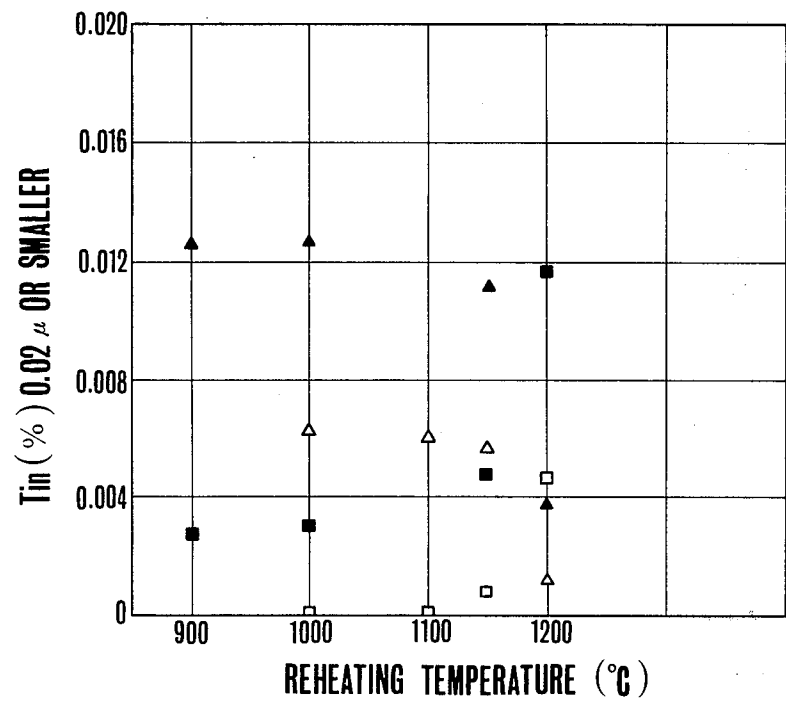
PLATE THICKNESS 32 mm (AS ROLLED)

FIG. 4



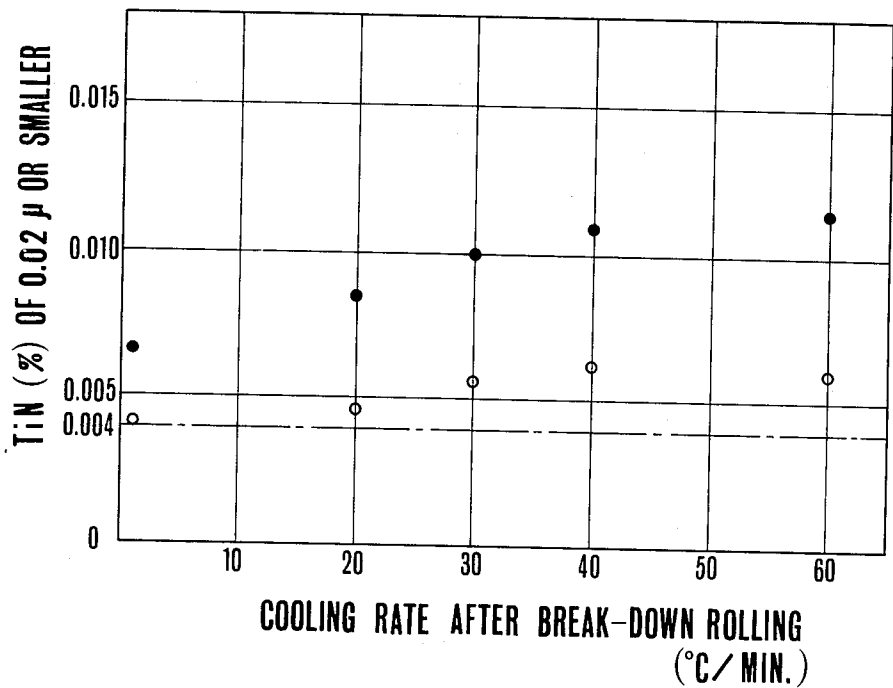
STEEL	NaS TiN / N	TiN OF 0.02 $\mu$ OR SMALLER
(2)-10	○	△
(2)-2	●	▲
HEATING CONDITIONS	T × 120' WQ	T × 120' WQ AND THEN 1150°C × 120' WC

FIG. 5



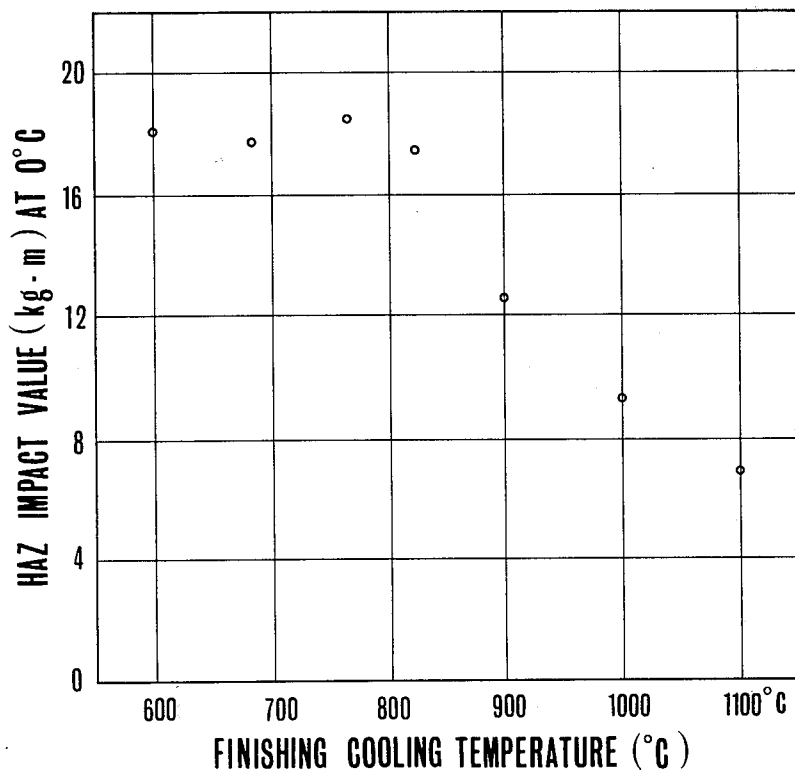
STEEL	Tin OF 0.02μ OR SMALLER	Tin BEYOND 0.02 μ
(2)- 10	△	□
(2)- 2	▲	■
HEATING CONDI- TIONS	1350°C×600'WG ( 60°C/min) T×200 REHEATING AC	

FIG. 6



STEEL	
(2) - 10	○
(2) - 2	●

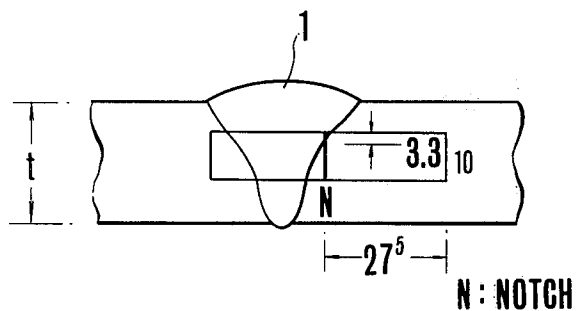
1350°C×600'&1150°C×200'AC  
FINISHING STRONG COOLING TEMPERATURE

**FIG. 7**

STEEL 1 PLATE THICKNESS 25mm

(1350°C × 600 MINUTES  
COOLING RATE 80°C / MIN.)COOLING RATE FROM FINISHING COOLING TEMPERATURE  
TO ORDINARY TEMPERATURE: 0.4°C / MIN.

WELDING METHOD: ELECTROSLAG WELDING

**FIG. 8**



## METHOD FOR PRODUCING STEEL MATERIALS FOR LARGE HEAT-INPUT WELDING

### BACKGROUND OF THE INVENTION

Requirements for welding materials have been becoming more and more severe in recent days and demands have been toward steel materials which are free from material deterioration at welded portions as well as from crackings during welding. Welding cracks generally occurs at welded portions by small heat-input welding while the material deterioration tends to increase as the heat-input for welding is increased. Thus, recent demands for welding materials are self-contradictory in that the above two phenomena which are completely contrary in respect of the heat-input must be simultaneously eliminated.

Therefore, an object of the present invention is to provide a method for producing high-toughness steel materials which satisfy the above demands.

### DETAILED EXPLANATION OF THE INVENTION

As for the requirements to the welding materials particularly in respect of welded portions, the followings should be satisfied generally.

1. Hardenability is small.
2. Cracking resistance is good enough.
3. Toughness deterioration is small.

As for the requirements (1) and (2), they are of particular concern in cases of small heat-input weldings, such as tack welding, upward welding and horizontal welding, etc.

Hardenability and cracking resistance are primarily depend on the chemical composition of the steel material to be welded and the heat-input for welding so far as the welding materials and welded structures are same, and thus generally determined by  $C_{eq}$  or  $P_c$  values as their parameters.

According to the present invention, the carbon content and the  $C_{eq}$  value are maintained low so as to obtain good properties in respect of the requirements (1) and (2), but the most remarkable feature of the present invention lies in that toughness deterioration in the weld-heat affected zone (hereinafter abridged as HAZ) is small. Thus the toughness deterioration in HAZ is practically negligible in the present invention if the heat-input increases up to 350 KJ/cm which is practical large heat-input in ordinary welding.

According to the conventionally known facts and knowledges, HAZ toughness strongly depends on the steel micro structure, and it is known that the best toughness is obtained when the structure is a low-carbon lower bainite.

In order to maintain the lower bainite structure at the time of welding, it is necessary to add a relatively large amount of alloying elements such as Ni and Mo for assuring strength and to widen the weld heat-input range which renders the HAZ structure into a lower bainite structure to a practically significant degree other than maintenance of the carbon content as low as possible. These requirements remarkably limit the utility field of welding materials having a lower bainite structure in the HAZ from both aspects of economy and the material strength (the material strength level is increased by the addition of alloying elements in a large amount).

The present invention has been developed for the purpose of eliminating the defects of conventional steels such that the heat-input is limited because of

hardening, cracking and toughness deterioration in HAZ, or that steel materials must be selected for each of applications of the welded structures, and the steel materials produced according to the present invention are practically free from toughness deterioration in HAZ and free from the above limitation in the welding operation.

#### Brief Explanation of the Drawings:

The present invention will be described in more details referring to the attached drawings.

FIG. 1 is a graph showing the relation between the austenite grain size number and 2 mm V notch Charpy impact test values at 0°C of the HAZ of joint portions by electroslag welding of the steel materials according to the present invention and comparative steel materials.

FIG. 2 is a graph showing the relation between 2 mm V notch Charpy impact values at 0°C of the HAZ of joint portions by electrogas welding and the amount of fine TiN up to 0.02 $\mu$  in the steel materials prior to welding in case of the steels containing 0.0015% N and 0.0036% N (Steels (2)-10 and (2)-2 in Table 2) according to the present invention.

FIG. 3 is a graph showing the relation between the heat-inputs between 2 mm V notch Charpy impact values at 0°C of HAZ of the steel (Steel (2)-10 in Table 2) according to the present invention and a comparative steel (Steel (2)-9 in Table 2) welded by various welding methods.

FIG. 4 is a graph showing the relation between the ratio of NaS TiN/N (those marked by  $\circ$  and  $\bullet$ ) in the steels (Steel (2)-10 and Steel (2)-2 in Table 2) of the present invention when they are heated at various temperatures and held at the temperatures for 120 minutes and rapidly cooled in water and the amount ( $\Delta$  and  $\blacktriangle$ ) of fine TiN up to 0.02 $\mu$  in the same steels when they are further held at 1150°C for 120 minutes and quenched in water.

FIG. 5 is a graph showing the relation between the amount of fine TiN up to 0.02 $\mu$  in the steels (Steels (2)-10 and (2)-2) according to the present invention when they are held at 1350°C for 600 minutes, subjected to breaking-down rolling, and cooled at a cooling rate of 60°C/mm, and then reheated to various temperatures (holding time: 200 minutes).

FIG. 6 is a graph showing the relation between the amount of the fine TiN ( $\Delta$  and  $\blacktriangle$  in the graph) and the cooling rate after the breaking down when the steels (Steels (2)-10 and (2)-2) according to the present invention were heated and held at 1350°C for 600 minutes, broken down, cooled at various cooling rates, and then heated and held at 1150°C for 200°C.

FIG. 7 is a graph showing the relation between the finishing cooling temperatures and the HAZ toughness (2 mm V notch Charpy test) when the steel (Steel 11 in Table 1) according to the present invention was heated and held at 1350°C for 600 minutes, broken down and water-cooled through the cooling course for stabilizing the HAZ toughness.

FIG. 8 shows the portion from which the 2mm V notch Charpy test pieces were taken for measuring the toughness values (vEo kg-m) of various welded joints as shown in Tables 1 to 6 (In the FIG. 1 is the deposited metal,  $t$  is the plate thickness).

The HAZ structure of conventional welding steel materials is not a lower-bainite structure, but mostly a mixture structure of martensite, lower-bainite, upper-

bainite, ferrite and pearlite, and toughness of HAZ strongly depends on the austenite grain size. Thus it is most important to control the austenite grain size as small as possible for prevention of the toughness deterioration in HAZ. As shown in FIG. 1, it is necessary to maintain the austenite grain size in the HAZ equal or larger than ASTM No. 0 in order to attain 2 mm V notch Charpy impact value of 4.2 kg-m or more at 0°C with a welding heat-input of 350 KJ/cm in case of a structure of pro-eutectoid ferrite + upper bainite which is commonly formed in a large heat-input welded HAZ of an ordinary structural steel.

As explained above, it is very effective to control the austenite grains in the HAZ as small as possible for improvement of the HAZ toughness, but in order to give industrial significance to this measure, selection of the steel composition which can maintain small austenite grains in the HAZ and limitation of production process are necessary.

The present inventors have conducted extensive studies on methods for controlling the austenite grain size in the HAZ, and found that it is effective to disperse fine TiN more than a certain amount in the steel prior to welding for the purpose. The present inventors have conducted further studies on methods for dispersing such fine TiN more than a certain amount, and developed a steel material which can give at least more than 4.2 kg-m 2 mm V notch Charpy impact value at 0°C to the HAZ by dispersing fine TiN more than a certain amount in the steel prior to welding by a method as described hereinafter other than the method disclosed in Japanese Patent Application Sho 45-25042, which comprises cooling rapidly the steel through the solidification course of the molten steel to precipitate fine TiN and subsequently heating the steel at a temperature which can avoid coarsening of TiN as much as possible to retain the fine TiN formed during the solidification cooling until the final steel products. (This method is most desirably done by a continuous casting method).

In other words, in case of Ti-containing steels produced by an ordinary steel-making method, TiN precipitates during the solidification of the steel ingot and coarsens during the solidification and the cooling so that it is almost impossible to adjust the size and amount of TiN in the subsequent steps. Therefore, as a method for obtaining a dispersion of fine TiN in Ti-containing steels, no method other than the method in which TiN precipitated during the solidification and cooling is finely dispersed, has been developed before the present invention.

The present inventors have succeeded in adjusting the size and amount of TiN by refining the coarse TiN in the subsequent steps. The adjustment has never been successful in the conventional arts.

According to the present invention, the amounts of Ti and N in the steel are limited, and the steel is heated to a temperature commonly adopted in an ordinary steel-making process to dissolve in solid solution TiN which was precipitated in the solidification and cooling in an amount not less than 0.004%, and this solid dissolved TiN is again reprecipitated as fine TiN of not larger than 0.02 $\mu$ .

Now the feature of the present invention lies in that:

#### 1. Basic Invention:

A method for producing steel materials suitable for large heat-input welding which comprises heating a

steel ingot or slab containing 0.03 to 1.18% C, 0.1 to 1.0% Si, 0.5 to 1.8% Mn, not more than 0.1% total Al, 0.004 to 0.03% Ti, 0.001 to 0.009% total N, with the balance being Fe and unavoidable impurities to a temperature between 1250° and 1400°C so as to dissolve into solid solution not less than 0.004% TiN, and then reprecipitating the dissolved TiN into fine TiN.

#### 2. First Modification:

A method for producing steel materials suitable for large heat-input welding, which comprises heating a steel ingot or slab containing 0.03 to 1.18% C, 0.1 to 1.0% Si, 0.5 to 1.8% Mn, not more than 0.1% total Al, 0.004 to 0.03% Ti, 0.001 to 0.009% total N, with the balance being Fe and unavoidable impurities to a temperature between 1250° and 1400°C so as to dissolve into solid solution not less than 0.004% TiN, rolling or forging the steel, forcedly cooling the steel to a temperature not higher than 800°C, and then reheating the steel to a temperature not higher than 1150°C so as to reprecipitate the dissolved TiN into fine TiN.

#### 3. Second Modification:

A method for producing steel materials suitable for large heat-input welding, which comprises heating a steel ingot or slab containing 0.03 to 0.18% C, 0.1 to 1.0% Si, 0.5 to 1.8% Mn, not more than 0.1% total Al, 0.004 to 0.03% Ti, 0.001 to 0.009% total N, with the balance being Fe and unavoidable impurities to a temperature between 1250° and 1400°C so as to dissolve into solid solution not less than 0.004% TiN, rolling or forging the steel with a finishing temperature not lower than 1000°C, and reheating the steel at a temperature not higher than 1150°C so as to reprecipitate the dissolved TiN into fine TiN.

#### 4. Third Modification:

A method for producing steel materials suitable for large heat-input welding, which comprises heating a steel ingot or slab containing 0.03 to 0.18% C, 0.1 to 1.0% Si, 0.5 to 1.8% Mn, not more than 0.1% total Al, 0.004 to 0.03% Ti, 0.001 to 0.009% total N, 0.001 to 0.03% REM with the balance being Fe and unavoidable impurities and satisfying the condition of REM/S = 1.0 to 6.0 to a temperature between 1250° and 1400°C so as to dissolve into solid solution not less than 0.004% TiN, and reprecipitating the dissolved TiN into fine TiN.

#### 5. Fourth Modification:

A method for producing steel materials suitable for large heat-input welding, which comprises heating a steel ingot or slab containing 0.03 to 0.18% C, 0.1 to 1.0% Si, 0.5 to 1.8% Mn, not more than 0.1% total Al, 0.004 to 0.03% Ti, 0.001 to 0.009% total N, one or more of not more than 0.05% Nb, not more than 0.08% V, and not more than 0.003% B with the balance being iron and unavoidable impurities to a temperature between 1250° and 1400°C so as to dissolve into solid solution not less than 0.004% TiN, and reprecipitating the dissolved TiN into fine TiN.

#### 6. Fifth Modification:

A method for producing steel materials suitable for large heat-input welding which comprises heating a steel ingot or slab containing 0.03 to 0.18% C, 0.1 to 1.0% Si, 0.5 to 1.8% Mn, not more than 0.1% total Al, 0.004 to 0.03% Ti, 0.001 to 0.009% total N, one or more of not more than 0.35% Cr, not more than 0.35% Mo, not more than 0.6% Cu, not more than 1.5% Ni, and not more than 1.0% W, with the balance being iron and unavoidable impurities and satisfying the condition

of  $(\text{Cu} + \text{Ni} + \text{W})/5 + \text{Cr} + \text{Mo} \leq 0.75\%$  to a temperature between  $1250^\circ$  and  $1400^\circ\text{C}$ , and reprecipitating the dissolved TiN into fine TiN.

#### 7. Sixth Modification:

In this modification 0.004 to 0.03% Ti is replaced by the same amount of one or more of Ti, Zr, and Hf so as to assure solid solution of nitrides in an amount of not less than 0.004% as one or more of TiN, ZrN and HfN during the heating step and reprecipitate fine TiN, ZrN and/or HfN.

The present invention will be described in more details hereinafter.

The features of the present invention in respect of the production process lie in that a heating step for dissolving not less than 0.004% of TiN which has been precipitated during the solidification and cooling is combined with a rolling or forging step for reprecipitating the dissolved TiN with or without reheating after the rolling or forging in the process for producing steel products by rolling or forging a Ti-containing steel ingot or slab prepared by an ordinary steel-making method, and in that grain growth of the austenite in the HAZ is restricted by means of the reprecipitated fine TiN so as to prevent the lowering of toughness.

In this case, if the content of Ti is excessive it is impossible to dissolve in solid solution 0.004% or more of the coarse TiN which has been precipitated during the solidification and cooling by an ordinary heating process. Therefore, in case of steels produced by an ordinary steel-making method, it is necessary to limit the content of Ti to 0.004 to 0.03%. Even in this case, if the heating temperature is excessively high, so-called burning phenomenon takes place so that there is a certain upper limit for the heating temperature, while the amount of Ti in solid solution depends on the heating temperature and time. In some cases, however, partial burning does not cause practical problem, and in case of the above-mentioned steel-making method based on the present steel making technics, it is necessary to limit the content of Ti up to 0.03%. On the other hand, the amount of Ti for assuring the lower limit of 0.004% of the fine TiN is 0.004% for the commercial purpose in view of some Ti which forms oxides and sulfides, etc. Thus the content of Ti should be 0.004 to 0.03%.

TiN which has been dissolved in solid solution precipitates during the rolling or forging and the subsequent cooling step, but the amount of Ti which remains in solid solution increases in some cases depending on the rolling, forging or cooling conditions. If this remaining Ti in solid solution is reprecipitated as TiN finely enough in the subsequent reheating step, the refinement of TiN is effectively stabilized particularly in case of a smaller content of TiN.

Descriptions will be made hereinafter on the heating temperature for dissolving the TiN which has been precipitated during the solidification and cooling of the molten steel, the reheating temperature and the limitations of the contents of N and TiN.

The steel materials obtained according to the present invention must have low hardenability and good crack resistance in the HAZ and also must be less susceptible to the HAZ toughness deterioration even when welded with a large heat-input up to about 350 KJ/cm. Therefore, the method according to the present invention is characterized in that TiN which has been precipitated during the solidification and cooling of the molten steel is once dissolved in solid solution by heating and then

reprecipitated into fine TiN so as to refine the austenite grains in the HAZ and to assure the HAZ toughness. In order to dissolve TiN into solid solution by such a heating process economically and stably on a commercial base, it is effective to limit not only the content of Ti but also the content of N so far as the present level of technology is concerned. The reason for defining the lower limit of N (total) to 0.001% is that the lower limit of the amount of TiN which must be dissolved into solid solution is 0.004% and the lower limit of N corresponds to this amount. On the other hand, it is disadvantageous if the upper limit of N (total) exceeds the equivalence to the upper limit of Ti for the purpose of assuring an enough amount of TiN which is dissolved into solid solution during the heating process so that the upper limit of N (total) is defined to 0.009% which is considered to correspond to 0.03% of Ti.

Meanwhile, when the amount of TiN exceeds 0.04%, the steel material toughness itself rather than the HAZ toughness is deteriorated, and thus it is necessary to define the upper limit of TiN to 0.04%, but so far as the amount of Ti and N (total) fall within the above range, the content of TiN never exceeds 0.04%.

When the contents of Ti and N are within the above mentioned range, the lower limit of the heating temperature for dissolving not less than 0.004% of TiN is  $1250^\circ\text{C}$  as shown in FIG. 4 which has been obtained by experiments. Meanwhile, as stated before, the upper limit is defined to  $1400^\circ\text{C}$  which is practically allowable in spite of partial burning due to iron oxides on the steel surface.

Regarding the upper limit of the reheating temperature for reprecipitating Ti and N remaining in solid solution, when the reheating temperature is above  $1150^\circ\text{C}$ , both the TiN which has been already precipitated and the TiN which is precipitated by the reheating become coarse and the amount of TiN not larger than  $0.02\mu$  decreases so that it is impossible to control the austenite grain size in the HAZ by the fine TiN. Thus the upper limit of the reheating temperature is defined to  $1150^\circ\text{C}$ .

The basic steel composition according to the present invention comprises 0.03 to 0.18% C, 0.1 to 1.0% Si, 0.5 to 1.8% Mn, not more than 0.1% total Al, 0.004 to 0.03% Ti, 0.001 to 0.009% total N with the balance being iron and unavoidable impurities.

The reasons for defining the components of the starting steel material will be explained hereinafter.

Less than 0.03% C does not give enough strength required by steel materials used for welding, and softening of the HAZ becomes considerable and large difference in strength is caused between the welded portions and the steel material when a large heat-input welding is applied so that the steel material is of no practical use. Thus the lower limit of the carbon content is defined to 0.03%. On the other hand, if the carbon content exceeds 0.18%, not only hardenability and cracking of the welded portions are remarkable, but also the HAZ toughness deteriorates because the grain refinement effect to the HAZ toughness is severely hindered by the hardening and thus the upper limit of the carbon content is defined to 0.18%.

Si is an element which is unavoidably contained in welding steels for reoxidation in steel making, but with less than 0.1% Si, notch toughness of the steel material lowers and thus the lower limit is defined to 0.1%. On the other hand, with an excessive content of Si, not

only the HAZ is embrittled but also the cleanliness of the steel itself is damaged. Thus the upper limit is defined to 1.0%.

Regarding the content of Mn, with less than 0.5% Mn, softening of the HAZ is remarkable and strength and toughness of the steel material itself lower so that no satisfactory welding steel material is obtained, and thus the lower limit of Mn is defined to 0.5%. On the other hand when the content of Mn is excessive, the HAZ toughness deteriorates sharply, and in case of the steel material as rolled the steel structure becomes upper bainite structure so that toughness lowers remarkably, and thus the upper limit of Mn is defined to 1.8%.

Al is an element which is unavoidably contained in Al-killed steels, but with more than 0.1% total Al, not only the HAZ toughness but also the toughness of the weld metal lower remarkably, and thus the upper limit of total Al is defined to 0.1%.

Regarding the contents of Ti and total N, the content of Ti is limited to from 0.004% to 0.03% and the content of total N is limited to from 0.001 to 0.009% for the reasons set forth hereinbefore. When Ti and N contents are within the above ranges, the content of TiN never exceeds 0.04%.

The steel according to the present invention contains P and S as impurities and normally contains less than 0.04% P, but P is not added intentionally in the present invention. S is normally contained in an amount less than 0.035%, and it is possible to lower the sulfur content down to about 0.0005% by the present level of technology, and in this case it is clear that both the HAZ toughness and the steel material toughness are improved. S is not added intentionally in the present invention.

According to the first modification of the present invention, the cooling conditions after the coarse TiN which has been precipitated during the solidification and cooling is dissolved by heating and the steel is rolled or forged are limited further. Thus, the cooling is effected forcibly by water or a mixture of water and gas, and the finishing temperature of this cooling is limited not higher than 800°C, so as to increase the amount of the fine TiN produced after the subsequent reheating at a temperature not higher than 1150°C. Therefore, when the starting basic steel is treated by the first modification of the present invention, the HAZ toughness is further stabilized, while other properties required by a welding steel materials are not sacrificed at all.

Some detailed explanations will be made hereinafter on the reason why the HAZ toughness is stabilized by the first modification of the present invention. As described before, the TiN which is once dissolved into solid solution by heating between 1250° and 1400°C precipitates again during the rolling or forging step and the subsequent cooling step. In this case, the amount and size of the precipitates are determined by the cooling rate as shown in FIG. 6. Thus, precipitates such as TiN which has a small supersaturation degree, not only precipitate during the cooling step but also coarsen if the cooling rate is relatively slow.

The first modification of the present invention has been made for overcoming the above defect, and comprises heating the basic steel as defined above to a high temperature between 1250° and 1400°C, rolling or forging the thus heated steel, forcibly cooling the

rolled or forged steel with water or a mixture of water and gas so as to render the size of TiN precipitating during the cooling as small as possible and to suppress the precipitation amount, and reheating the steel to precipitate fine TiN not larger than 0.02 $\mu$  as much as possible so as to further stabilize the HAZ toughness. In this case, the finishing cooling temperature should be not higher than 800°C for the reason that it is a temperature range above 800°C which contributes substantially to the TiN precipitation and growth in case of a continuous cooling. Within the temperature range below 800°C, the amount of the precipitates is small and the size is also small so that the precipitates do not coarsen during the subsequent reheating step at a temperature below 1150°C and do not effect the amount of the fine TiN of 0.02 $\mu$  or smaller. It is effective for stabilizing the HAZ toughness if the cooling after the working is forced effected according to the first modification of the present invention to suppress the coarsening of TiN when the steel is worked, and further the steel slab is heated between 1250° and 1400°C when it is worked into a final steel product, because the dissolution of TiN during the second heating promoted by the first heating and the forced cooling in combination, and thus the amount of the fine TiN in the final steel product is increased.

According to the second modification of the present invention, the conditions of the rolling or forging the steel after the coarse TiN which has been precipitated during the solidification and cooling is dissolved are further limited. Thus, by limiting the finishing working temperature to 1000°C or higher, the amount of the fine TiN produced after the reheating at a temperature not higher than 1150°C can be increased, and the HAZ toughness can be still further stabilized.

Although the technical means of the second modification is different from that of the first modification but the both modifications are metallurgically same in that the production conditions after the dissolving heating are particularly limited to suppress the precipitation of the coarse TiN before the reheating as much as possible to precipitate the fine TiN of 0.02 $\mu$  or smaller as much as possible after the reheating.

According to the second modification of the present invention, the finishing working temperature is not lower than 1000°C so that the formation of TiN precipitation nuclei during the rolling or forging is reduced and thus TiN precipitation during the subsequent cooling is reduced and also the precipitation of the coarse TiN is suppressed. Therefore, the second modification brings forth the same results as the first modification and stabilizes still further the HAZ toughness. It is very natural that if the second modification is combined with the first modification, the HAZ toughness is still further stabilized.

According to the third modification of the present invention, rare earth metals (REM), chiefly Ce, La and Pr, are added to the basic steel composition, in an amount between 0.001 to 0.03%, and the ratio of REM/S is defined to from 1.0 to 6.0. As shown in Table 4, the HAZ toughness of the steel treated according to the third modification is further stabilized. Regarding the contents of REM, with a content less than 0.001%, no practical effect for improving the HAZ toughness and the steel material toughness is attained, and on the other hand, with a content beyond 0.03%, REM-sulfides grow larger and a large amount of REM-

oxysulfides is produced to form large-size inclusions, thus remarkably damaging the steel material toughness and the cleanliness of the steel. For this reason, the content of REM is limited to from 0.001 to 0.03%. Meanwhile, REM is effective in correlation with S content for improving and stabilizing the HAZ toughness and the steel material toughness, and the optimum range of REM content is from 1.0 to 6.0 based on REM/S. It is natural that if the third modification of the present invention is combined with either the first or second modification or both the HAZ toughness is still further stabilized.

According to the fourth modification of the present invention, one or more of not more than 0.05% Nb, not more than 0.08% V and not more than 0.003% B is further added to the basic steel composition. These elements are added for the purpose of further improving the strength and toughness of the steel produced by the present invention as well as widening the plate thickness range which can be commercially produced and assuring the strength of the joints welded with a large heat-input. If these elements are added in an excessive amount, the HAZ toughness is remarkably deteriorated even in case of a steel in which the HAZ toughness has been improved by the fine TiN as in the steel produced according to the present invention. Therefore, their upper limits are defined.

Nb contents up to 0.05% improves the above various properties without substantially deteriorating the HAZ toughness, but Nb contents beyond 0.05% remarkably deteriorate the HAZ toughness. Therefore, the upper limit is defined to 0.05%.

V has similar effects as Nb, but its upper limit is allowed to 0.08%.

B is a useful element when the steel produced by the present invention is quenched and tempered, but when it is added in an amount beyond 0.003% B-constituent is formed in the HAZ at the time of a large heat-input welding, and the HAZ toughness is remarkably deteriorated. Thus the upper limit of B is defined to 0.003%.

Meanwhile, experiments have been conducted by the present inventors on the combined addition of these elements, and it has been found that no deterioration of the HAZ toughness is caused by the combined addition, and the advantages and the features of the steel produced by the present invention are not damaged. It is also natural that if the fourth modification of the present invention is combined with one or more of the first, second and third modifications, the HAZ toughness is still further stabilized.

According to the fifth modification of the present invention, one or more of not more than 0.35% Cr, not more than 0.35% Mo, not more than 1.5% Ni, not more than 0.6% Cu and not more than 1.0% W is further added to the basic steel composition so as to satisfy the

condition:  $(\text{Cu} + \text{Ni} + \text{W})/5 + \text{Cr} + \text{Mo} \leq 0.75\%$ .

These elements are added to the basic steel composition for the purpose of improving the steel material strength and toughness and widening the plate thickness range which is permitted in the commercial production without substantially sacrificing the HAZ toughness, and their contents are naturally limited.

Regarding Cr, an excessive chromium content will increase hardenability of the HAZ and lower the HAZ toughness and crack resistance. Thus the upper limit is defined to 0.35%.

Mo is similar to Cr and effective to improve various properties of the steel material, but its upper limit is defined to 0.35% because of its adverse effect on the HAZ.

Ni is effective to increase the strength and toughness of the steel material without adverse effect on the HAZ hardenability and toughness, but a nickel content beyond 1.5% will cause adverse effect on the HAZ hardenability and toughness, and thus its upper limit is defined to 1.5%.

Regarding Cu and W, they have similar effects as Ni and are useful for corrosion resistance, but a copper content beyond 0.6% will cause Cu-crack during the rolling or forging step of the steel material. Thus the upper limit is defined to 0.6%. On the other hand, a tungsten content beyond 1.0% will cause deterioration of the HAZ toughness and increased hardenability, and thus the upper limit is defined to 1.0%.

Further these elements are added within the above ranges under the condition of  $(\text{Cu} + \text{Ni} + \text{W})/5 + \text{Cr} + \text{Mo} \leq 0.75\%$ . If this condition is not satisfied, the HAZ hardness is remarkably increased and cracks occur in the HAZ during the small heat-input welding.

It is natural that when the steel composition of the fifth modification is applied to one or more of the first, second and third modifications of the present invention, the HAZ toughness is still further stabilized, and it is also possible to apply the fourth modification to the steel composition of the fifth modification.

According to the sixth modification of the present invention, 0.004 to 0.03% Ti is replaced by 0.004 to 0.03% of one or more than two of Ti, Zr and Hf. Zr and Hf are elements belonging to the same group as Ti and form stable nitrides just as Ti, prevent coarsening of the austenite grain size in the HAZ and improve the HAZ toughness. Therefore, if one or more than two of Ti, Zr and Hf is added in an amount from 0.04 to 0.03% so as to dissolve into solid solution not less than 0.004% of one or more than two of TiN, ZrN and HfN and then reprecipitates them, the same effects as obtained by Ti can be obtained. The elements other than Ti, Zr and Hf are limited to the same ranges as defined in the previous modifications for the same reasons.

Examples of the present invention are shown in Tables 1 to 7.

TABLE 1

Steel No.	Example of Group 1 of the Present Invention															Producing Conditions		
	C	Si	Mn	Ti	Chemical Composition (%)										1)	2)	3)	
					Al	N	B	V	Nb	Ni	Cu	Cr	Mo	W	Ceq	CM	TiN up to	
					total	total									(%)	(%)	0.02μ	
Present Invention																		
1	0.12	0.23	0.50	0.012	0.025	0.0048	—	—	—	—	—	—	—	—	0.203	0	0.0048	
2	0.14	0.25	1.75	0.004	0.016	0.0051	—	—	—	—	—	—	—	—	0.432	0	0.0040	
3	0.04	0.48	1.45	0.025	0.031	0.0036	—	—	—	—	—	—	—	—	0.282	0	0.0056	
4	0.04	0.48	1.45	0.025	0.031	0.0036	—	—	—	—	—	—	—	—	0.282	0	0.0044	

TABLE 1 -Continued

Example of Group 1 of the Present Invention																	
Steel No.	Chemical Composition (%)														Producing Conditions		
	C	Si	Mn	Ti	Al total	N total	B	V	Nb	Ni	Cu	Cr	Mo	W	1)	2)	3)
															Ceq (%)	CM (%)	TiN up to 0.02μ (%)
Comparative Steels																	
5	0.04	0.48	1.45	0.025	0.031	0.0036	—	—	—	—	—	—	—	—	0.282	0	0.0008
6	0.13	0.25	1.30	—	0.031	0.0052	—	—	—	—	—	—	—	—	0.347	0	—
7	0.13	0.25	1.30	—	0.031	0.0052	—	—	—	—	—	—	—	—	0.347	0	—
8	0.16	0.31	0.95	0.025	0.018	0.0062	—	—	—	—	—	—	—	—	0.318	0	0.0004
9	0.15	0.25	1.37	0.050	0.037	0.0102	—	—	—	—	—	—	—	—	0.378	0	0.0014
10	0.15	0.25	1.37	0.050	0.037	0.0102	—	—	—	—	—	—	—	—	0.378	0	0.0015
Steel No.	Soaking Temp. (°C)	Cooling Rate (°C/mm)	Producing Conditions		Heat Treatment	Plate Thick-ness (mm)	Material Properties			Elonga-tion (%)							
			Heating Temp. for Rolling (°C)	Cooling Rate in Rolling (°C/sec.)			Yield Point (kg/mm <sup>2</sup> )	Tensile Strength (kg/mm <sup>2</sup> )									
Present Invention																	
1	1350	1.0	1150	1.2	AR	32	24.8	43.1	48								
2	1300	1.0	1100	2.1	QT	25	59.0	68.3	24								
3	1350	50	1150	1.2	N 32	23.6	41.8	53									
4	—	—	1350	1.2	QT	32	47.3	62.4	28								
Comparative Steels																	
5	—	—	1150	1.2	QT	32	46.3	63.1	28								
6	1350	50	1150	1.2	AR	32	34.0	52.1	36								
7	1350	1.0	1250	2.1	QT	25	48.7	61.0	27								
8	1200	1.0	1150	1.2	AR	32	26.0	45.7	32								
9	1350	1.0	1100	1.2	AR	32	43.7	62.0	24								
10	1350	1.0	1100	2.1	QT	25	51.2	64.8	26								
Steel No.	Material Properties		Maximum Hardness (JISZ 3101)	Welding Properties		Welding Method and Heat Input	vEo (kg-m)										
	vE-10 (kg-m)	vTrs (°C)		Toughness of HAZ of Shielded Arc Welded Joint (Manual Welding) vEo (kg-m)	Toughness of Large Heat-Input Welded Joint												
1	27.6	−20	210	21.4	(KJ/cm) SAW 220	10.1											
2	18.9	−45	385	18.2	EG 150	8.6											
3	36.2	−65	240	32.5	ES 345	11.8											
4	40.3	−90	243	34.5	EG 190	9.3											
5	38.7	−85	248	22.3	EG 190	2.1											
6	10.9	−25	320	13.2	SAW 220	1.8											
7	19.3	−40	315	18.7	EG 150	2.8											
8	10.6	0	330	10.2	SAW 220	3.8											
9	6.7	+ 5	375	12.0	ES 327	2.7											
10	19.3	−15	358	16.3	EG 150	3.1											

1)  $Ceq = C + \frac{1}{6} Mn + \frac{1}{5} Cr + \frac{1}{4} Mo + \frac{1}{40} (Ni + Cu + W) + \frac{1}{14} V$

2)  $CM = \frac{1}{5} (Cu + Ni + W) + Cr + Mo$

- 3) Values of steel materials before welding.
- 4) SAW: Submerged arc welding; EG: Electroslag welding; ES: Electroslag welding.

TABLE 2

Example of Group 2 of the Present Invention																		
Steel No.	C	Si	Mn	Ti	Chemical Composition (%)										Producing Conditions			
					Al total	N total	B	V	No	Ni	Cu	Cr	Mo	W	Ceq (%)	CM (%)	TiN up to 0.02μ(%)	
Pre-sent Inven-tion	(2)-1	0.12	0.25	1.38	0.013	0.035	0.0036	—	—	—	—	—	—	—	—	0.350	0	0.0100
	(2)-2	0.12	0.25	1.38	0.013	0.035	0.0036	—	—	—	—	—	—	—	—	0.350	0	0.0118
	(2)-3	0.12	0.25	1.38	0.013	0.035	0.0036	—	—	—	—	—	—	—	—	0.350	0	0.0116
	(2)-4	0.12	0.25	1.38	0.013	0.035	0.0036	—	—	—	—	—	—	—	—	0.350	0	0.0081
	(2)-5	0.12	0.25	1.38	0.013	0.035	0.0036	—	—	—	—	—	—	—	—	0.350	0	0.0042
	(2)-6	0.13	0.25	1.45	0.014	0.038	0.0090	—	—	—	—	—	—	—	—	0.372	0	0.0045
	(2)-7	0.13	0.25	1.45	0.014	0.038	0.0090	—	—	—	—	—	—	—	—	0.372	0	0.0042

TABLE 2--Continued

Example of Group 2 of the Present Invention																		
Steel No.	C	Si	Mn	Ti	Chemical Composition (%)										Producing Conditions			
					Al total	N total	B	V	No	Ni	Cu	Cr	Mo	W	Ceq (%)	CM (%)	TiN up to 0.02μ(%)	
Com-pa-rative Steels Present Inven-tion	(2)-8	0.14	0.27	1.35	0.040	0.027	0.0037	—	—	—	—	—	—	—	0.365	0	0.0033	
	(2)-9	0.13	0.25	1.36	—	0.038	0.0051	—	—	—	—	—	—	—	0.357	0	—	
	(2)-10	0.12	0.37	1.45	0.012	0.033	0.0015	—	—	—	—	—	—	—	0.362	0	0.0059	
Steel No.	Producing Conditions										Material Properties							
	Soaking Temp. (°C)	Cooling Rate (°C/mm)	Finishing Accelerated Cooling Temp. (°C)	Heating Temp. for Rolling (°C)	Cooling Rate in Rolling (°C/sec.)	Heat Treat-ment	Plate Thick-ness (mm)	Yield Point (kg/mm <sup>2</sup> )	Tensile Strength (kg/mm <sup>2</sup> )	Elong-ation (%)	vE-10 (kg-m)	vTrs (°C)						
(2)-1	1350	60	1100	1150	1.2	AR	32	31.3	47.3	48	17.4	-15						
(2)-2	1350	50	800	1150	1.2	AR	32	33.1	48.3	43	19.3	-28						
(2)-3	1350	50	800	1150	1.2	QT	32	47.2	59.3	28	20.8	-45						
(2)-4	1350	0.15	—	1150	1.2	AR	32	31.3	46.7	47	18.2	-20						
(2)-5	1350	0.15	—	1250	1.2	AR	32	30.6	45.3	48	13.3	0						
(2)-6	1350	60	800	1150	1.2	AR	32	33.0	49.8	40	28.3	-40						
(2)-7	1350	50	1050	1150	1.2	AR	32	33.8	50.2	42	24.1	-45						
(2)-8	1350	50	800	1150	1.2	AR	32	44.2	63.5	23	3.1	+15						
(2)-9	1350	50	800	1150	1.2	AR	32	34.3	50.6	39	14.3	0						
(2)-10	1350	60	800	1150	1.2	AR	32	33.4	50.2	48	28.3	-40						
Steel No.	Welding Properties																	
	Maximum Hardness (JISZ 3101)	Toughness of HAZ of Shielded Arc (Manual Welding) Welded Joint vEo (kg-m)			Toughness of Large Heat-Input Welded Joint Welding Method and Heat Input (KJ/cm) vEo (kg-m)													
(2)-1	342	19.3			ES 320 13.9													
(2)-2	328	18.3			ES 320 18.7													
(2)-3	350	17.9			EG 190 16.3													
(2)-4	321	20.4			ES 320 11.7													
(2)-5	335	16.4			ES 320 4.3													
(2)-6	390	14.8			ES 320 9.3													
(2)-7	386	16.1			ES 320 7.9													
(2)-8	355	10.4			ES 320 3.7													
(2)-9	341	13.8			ES 320 1.8													
(2)-10	333	18.0			ES 320 10.2													

TABLE 3

Examples of Group 3 of the Present Invention																		
Steel No.	C	Si	Mn	Ti	Chemical Composition (%)										Producing Conditions			
					Al total	N total	B	V	Nb	Ni	Cu	Cr	Mo	W	Ceq (%)	CM (%)	TiN up to 0.02μ (%)	Soaking Temp. (°C)
Steels of Present Invention																		
(3)-1	0.12	0.27	1.35	0.012	0.028	0.0035	—	—	—	—	—	—	—	—	0.356	0	0.0086	1350
(3)-2	0.12	0.27	1.35	0.012	0.028	0.0035	—	—	—	—	—	—	—	—	0.356	0	0.0065	1350
(3)-3	0.12	0.27	1.35	0.012	0.028	0.0035	—	—	—	—	—	—	—	—	0.356	0	0.0061	1350
(3)-4	0.12	0.27	1.35	0.012	0.028	0.0035	—	—	—	—	—	—	—	—	0.356	0	0.0054	1350
(3)-5	0.12	0.27	1.35	0.012	0.028	0.0035	—	—	—	—	—	—	—	—	0.356	0	0.0113	1350
Comp. Steel																		
(3)-6	0.13	0.25	1.31	0.043	0.026	0.0048	—	—	—	—	—	—	—	—	0.358	0	0.0027	1350
Steel No.	Producing Conditions										Material Properties							
	Finishing	Cooling	Finishing	Heating	Finishing	Cooling	Heat-	Plate	Yield	Tensile Strength	Elonga-	vE-10	vTrs					
	Temp.	Rate	Accelerated Cooling	Temp. Rolling	Temp. Rolling	ment	ness	Thick-	Point					tion	(°C)			
	(°C)	(°C/mm)	Temp.(°C)		(°C)	(°C/sec)		(kg/mm <sup>2</sup> )	(kg/mm <sup>2</sup> )									
								(mm)										
											g-m (%)							
(3)-1	1100	1.0	—	1150	970	1.2	AR	32	31.5	46.9	46	13.6	—5					
(3)-2	1050	1.0	—	1250	1050	1.2	N	32	32.1	47.3	47	23.5	—40					
(3)-3	1050	1.0	—	1250	1000	1.2	N	32	32.4	47.6	47	25.1	—45					
(3)-4	1050	1.0	—	1250	900	1.2	N	32	32.7	47.8	45	25.8	—40					
(3)-5	1050	50	800	1150	965	1.2	N	32	32.5	47.5	46	26.3	—45					
(3)-6	1050	1.0	—	1250	1050	1.2	N	32	32.6	47.9	46	25.9	—35					

TABLE 3—Continued

Steel No.	Maximum Hardness (JISZ 3101)	Welding Properties		
		Toughness of HAZ of Shielded Arc (Manual Welding) Welded Joint vEo (kg-m)	Toughness of Large Heat-Input Welded Joint Welding Method and Heat Input (KJ/cm)	
(3)-1	332	15.0	ES 320	12.3
(3)-2	328	17.8	ES 320	11.2
(3)-3	326	18.3	ES 320	10.7
(3)-4	332	16.9	ES 320	9.8
(3)-5	329	18.5	ES 320	15.4
(3)-6	347	10.5	ES 320	2.1

TABLE 4

Examples of Group 4 of the Present Invention

Steel No.	Chemical Composition (%)													REM/S
	C	Si	Mn	Ti	Al total	N total	S	V	Nb	Ni	Cu	Cr	REM	
Present Invention														
(4)-1	0.14	0.27	1.37	0.010	0.040	0.0041	0.002	—	—	—	—	—	0	0
(4)-2	0.14	0.27	1.37	0.010	0.040	0.0041	0.002	—	—	—	—	—	0.002	1
(4)-3	0.14	0.27	1.37	0.010	0.040	0.0041	0.002	—	—	—	—	—	0.008	4
(4)-4	0.14	0.27	1.37	0.010	0.040	0.0041	0.002	—	—	—	—	—	0.008	4
Comp. Steel														
(4)-5	0.12	0.29	1.45	—	0.038	0.0051	0.004	—	—	—	—	—	0.004	1
Producing Conditions														
	Ceq (%)	CM (%)	TiN up to 0.02μ(%)											
(4)-1	0.368	0	0.0064											
(4)-2	0.368	0	0.0067											
(4)-3	0.368	0	0.0061											
(4)-4	0.368	0	0.0094											
(4)-5	0.362	0	---											
Steel No.	Soak-ing Temp. (°C)	Cooling Rate (°C/mm)	Producing Conditions		Heat Treatment	Plate Thick-ness (mm)	Yield Point (kg/mm <sup>2</sup> )	Material Properties				vE-10 (kg-m)	vTrs (°C)	
			Heating Temp. for Rolling (°C)	Cooling Rate in Rolling (°C/sec)				Tensile Strength (kg/mm <sup>2</sup> )	Elonga-tion (%)					
(4)-1	1350	0.6	1150	1.2	AR	32	34.1	50.6	40		15.7	-20		
(4)-2	1350	0.6	1150	1.2	AR	32	33.7	49.8	43		16.9	-30		
(4)-3	1350	0.6	1150	1.2	AR	32	24.1	51.7	41		20.8	-30		
(4)-4	1350	50	1150	1.2	AR	32	33.8	51.0	43		22.1	-30		
(4)-5	1350	50	1150	1.2	AR	32	34.0	52.3	41		18.0	-25		
Steel No.	Maximum Hardness (JISZ 3101)	Welding Properties			Toughness of Large Heat-Input									
		Toughness of HAZ of Shielded Arc (Manual Welding) Welded Joint vEo (kg-m)	Welded Joint Welding Method and Heat Input (KJ/cm)		vEo (kg-m)									
(4)-1	375	17.3	EG 190	13.7										
(4)-2	380	18.3	EG 190	16.3										
(4)-3	367	16.2	EG 190	15.2										
(4)-4	377	17.3	EG 190	21.3										
(4)-5	342	10.8	EG 190	1.9										

TABLE 5

Examples of Group 5 of the Present Invention

Steel No.	C	Si	Mn	Ti	Chemical Composition (%)										Producing Conditions		
					Al total	N total	B	V	Nb	Cu	Cr	Mo	W	Ceq (%)	CM (%)	TiN up to 0.02μ(%)	
*	(5)-1	0.14	0.35	1.25	0.008	0.030	0.0025	—	—	0.03	—	—	—	—	0.348	0	0.0057
*	(5)-2	0.14	0.35	1.25	0.008	0.030	0.0025	—	—	0.05	—	—	—	—	0.348	0	0.0055
**	(5)-3	0.14	0.35	1.25	0.008	0.030	0.0025	—	—	0.08	—	—	—	—	0.348	0	0.0052
*	(5)-4	0.16	0.27	1.35	0.014	0.021	0.0042	—	0.06	—	—	—	—	—	0.397	0	0.0052
**	(5)-5	0.16	0.27	1.35	0.014	0.021	0.0042	—	0.10	—	—	—	—	—	0.405	0	0.0058
*	(5)-6	0.12	0.45	1.50	0.018	0.040	0.0059	—	0.03	0.03	—	—	—	—	0.378	0	0.0053
*	(5)-7	0.15	0.43	1.60	0.011	0.024	0.0060	—	0.02	0.03	—	—	—	—	0.330	0	0.0058
*	(5)-8	0.13	0.27	1.37	0.012	0.031	0.0048	0.0008	—	—	—	—	—	—	0.358	0	0.0049
**	(5)-9	0.13	0.27	1.37	0.012	0.031	0.0048	0.0038	—	—	—	—	—	—	0.358	0	0.0044
*	(5)-10	0.14	0.18	1.27	0.014	0.027	0.0038	0.0009	0.02	0.03	—	—	—	—	0.356	0	0.0091



TABLE 5—Continued

Steel No.	Soaking Temp. (°C)	Producing Conditions			Plate Thickness (mm)	Yield Point (kg/mm <sup>2</sup> )	Material Properties			
		Cooling Rate (°C/mm)	Heating Temp. for Rolling (°C)	Heat Treatment			Tensile Strength (kg/mm <sup>2</sup> )	Elongation (%)	vE-10 (kg-m)	vTrs (°C)
(5)-1	1300	0.6	1150	AR	20	40.3	56.2	38	12.6	-35
(5)-2	1300	0.6	1150	AR	20	46.6	60.1	37	18.1	-45
(5)-3	1300	0.6	1150	AR	20	40.2	54.3	42	11.6	-60
(5)-4	1320	0.6	1150	AR	20	38.0	56.1	32	12.1	-20
(5)-5	1320	0.6	1150	AR	20	40.2	57.1	28	7.5	0
(5)-6	1350	0.6	1150	AR	20	39.4	52.8	39	19.3	-40
(5)-7	1350	50	1150	AR	20	43.2	57.6	39	20.6	-45
(5)-8	1350	0.6	1150	QT	25	46.1	61.8	27	14.8	-45
(5)-9	1350	0.6	1150	QT	25	46.9	62.1	22	10.8	-25
(5)-10	1370	0.6	1150	QT	25	53.1	64.8	27	18.3	-60

Steel No.	Maximum Hardness (JISZ 3101)	Welding Properties		Toughness of Large Heat-Input Welded Joint	
		Toughness of HAZ of Shielded Arc (Manual Welding) Welded Joint vEo (kg-m)		Welding Method and Heat Input (KJ/cm)	vEo (kg-m)
(5)-1	230	16.2	SAW	90	10.7
(5)-2	240	14.8		90	6.8
(5)-3	260	13.6		90	3.6
(5)-4	280	10.3		90	8.1
(5)-5	290	8.7		90	2.9
(5)-6	240	12.3		90	6.7
(5)-7	340	12.3		90	6.7
(5)-8	370	18.1	EG	150	14.3
(5)-9	375	14.6		150	3.9
(5)-10	356	17.3		150	11.2

\* =Steels of Present Invention

\*\* =Comparative Steel

\* Remark: (5)-7 was subjected to accelerated cooling to 800°C.

TABLE 6

Example of Group 6 of the Present Invention

Steel No.	C	Si	Chemical Composition (%)				B	V	Nb
			Mn	Ti	Al total	N total			
Present Invention									
(6)- 1	0.15	0.15	0.87	0.018	0.012	0.0037	—	—	—
(6)- 2	0.14	0.25	0.87	0.020	0.022	0.0052	—	—	—
(6)- 3	0.12	0.34	1.20	0.014	0.027	0.0061	—	—	—
(6)- 4	0.16	0.30	1.15	0.020	0.043	0.0047	—	—	—
(6)- 5	0.17	0.21	0.98	0.010	0.011	0.0080	—	—	—
(6)- 6	0.09	0.31	0.59	0.014	0.021	0.0040	—	—	—
(6)- 7	0.09	0.21	0.67	0.023	0.045	0.0072	—	—	—
(6)- 8	0.12	0.18	0.92	0.007	0.013	0.0061	—	—	—
(6)- 9	0.13	0.28	1.25	0.011	0.043	0.0038	—	—	—
(6)-10	0.07	0.31	0.98	0.019	0.021	0.0051	—	—	—
(6)-11	0.18	0.31	0.53	0.016	0.047	0.0031	—	—	—
(6)-12	0.11	0.17	0.92	0.020	0.011	0.0047	—	—	—
(6)-13	0.09	0.25	0.75	0.013	0.021	0.0033	—	—	—
(6)-14	0.07	0.21	1.30	0.017	0.041	0.0039	—	—	—
(6)-15	0.14	0.17	1.21	0.012	0.029	0.0041	—	—	—
Comp. Steel									
(6)-16	0.13	0.27	1.40	0.011	0.033	0.0051	—	—	—
Present Invention									
(6)-17	0.14	0.27	1.27	0.013	0.013	0.0033	—	0.03	—
(6)-18	0.13	0.21	1.31	0.021	0.037	0.0046	0.0010	0.04	—

TABLE 6—Continued

Steel No.	Chemical Composition (%)					Producing Conditions		
	Ni	Cu	Cr	Mo	W (%)	Ceq (%)	CM 0.02μ (%)	TiN up to
(6)-1	—	—	0.34	—	—	0.363	0.340	0.0051
(6)-2	—	—	—	0.30	—	0.360	0.300	0.0052
(6)-3	1.30	—	—	—	—	0.352	0.260	0.0070
(6)-4	—	0.50	—	—	—	0.364	0.100	0.0049
(6)-5	—	—	—	—	0.40	0.343	0.080	0.0048
(6)-6	—	—	0.25	0.13	—	0.272	0.380	0.0059
(6)-7	0.81	—	0.31	—	—	0.284	0.472	0.0053
(6)-8	—	0.31	0.21	—	—	0.333	0.272	0.0052
(6)-9	—	—	0.12	—	0.40	0.372	0.210	0.0071
(6)-10	—	—	—	0.31	0.50	0.320	0.410	0.0096
(6)-11	—	0.30	—	0.10	—	0.301	0.150	0.0067
(6)-12	1.30	—	—	0.09	—	0.317	0.35	0.0044
(6)-13	0.80	0.20	—	0.15	—	0.278	0.35	0.0079
(6)-14	—	0.18	0.20	0.10	0.40	0.366	0.416	0.0050
(6)-15	0.25	—	—	0.10	0.30	0.370	0.21	0.0071
(6)-16	1.25	—	0.31	0.28	—	0.526	0.84	0.0067
(6)-17	0.80	—	—	0.10	—	0.404	0.26	0.0116
(6)-18	0.20	—	—	0.15	—	0.390	0.19	0.0080

Steel No.	Soak-ing Temp. (°C)	Producing Conditions			Plate Thick-ness (mm)	Material Properties		
		Cool-ing Rate (°C/mm)	Heating Temp.for Rolling (°C)	Heat-Treat-ment		Yield Point (kg/mm <sup>2</sup> )	Tensile Strength (kg/mm <sup>2</sup> )	Elon-gation (%)
(6)-1	1350	1.0	1150	AR	25	28.0	44.3	46
(6)-2	1350	1.0	1150	AR	25	30.2	47.6	32
(6)-3	1350	50	1150	N	25	39.3	52.4	39
(6)-4	1350	1.0	1150	AR	25	32.4	50.1	40
(6)-5	1350	50	1150	AR	25	30.0	47.2	39
(6)-6	1350	1.0	1150	N	25	22.7	40.8	47
(6)-7	1350	1.0	1150	N	25	23.0	44.1	48
(6)-8	1350	1.0	1150	AR	25	28.3	42.0	46
(6)-9	1350	1.0	1150	N	25	32.0	47.3	42
(6)-10	1350	50	1150	QT	25	47.0	56.9	28
(6)-11	1350	1.0	1150	QT	25	42.6	54.3	27
(6)-12	1350	1.0	1150	N	25	33.0	50.7	42
(6)-13	1350	1.0	1150	N	25	33.2	51.0	43
(6)-14	1350	1.0	1150	QT	25	52.3	63.1	24
(6)-15	1350	1.0	1150	QT	25	54.3	64.5	22
(6)-16	1350	50	1150	QT	25	63.2	75.3	22
(6)-17	1350	50	1150	QT	25	60.2	71.3	21
(6)-18	1350	50	1150	QT	25	64.8	77.4	20

Steel No.	Material Properties		Maximum Hardness (JIS Z 3101)	Welding Properties		Toughness of Large heat-Input Welded Joint	
	vE-10 (kg-m)	vTrs (°C)		Toughness of HAZ of Shielded Arc (Manual Weld-ing) Welded Joint vEo (kg-m)	Welding Method and Heat Input (KJ/cm)	vEo (kg-m)	
(6)-1	12.1	-40	325	12.1	SAW	90	9.2
(6)-2	9.8	-15	378	9.8		90	7.5
(6)-3	17.6	-90	316	17.2		90	14.9
(6)-4	12.7	-25	323	17.9		90	12.3
(6)-5	19.2	-20	314	13.2		90	14.2
(6)-6	29.3	-40	265	20.6		150	10.1
(6)-7	30.6	-60	235	24.3	EG	150	10.4
(6)-8	19.3	-25	301	16.2		90	15.0
(6)-9	20.9	-35	352	18.2		90	18.7
(6)-10	38.0	-80	241	20.6		150	11.4
(6)-11	26.3	-45	340	9.6		150	10.8
(6)-12	19.7	-50	295	17.1		150	9.0
(6)-13	18.7	-50	270	23.4	EG	150	14.7
(6)-14	26.3	-65	298	22.7		150	8.2
(6)-15	19.3	-65	350	14.3		150	13.3
(6)-16	12.3	-80	422	10.6		150	4.3
(6)-17	18.3	-45	408	9.9		150	10.6
(6)-18	14.6	-80	392	13.1		150	12.7

\* Remark: (6)-5, (6)-10, (6)-16-18 was subjected to accelerated cooling to 800°C.

TABLE 7

Examples of Group 7 of the Present Invention													
Steel No.	C	Si	Mn	Ti	Chemical Composition (%)					N total	V	Nb	Ni
					Zr	Hf	Al total						
Present Invention	(7)-1	0.12	0.28	1.36	—	0.011	—	0.029	0.0018	—	—	—	
	(7)-2	0.12	0.28	1.36	—	0.011	—	0.029	0.0018	—	—	—	
	(7)-3	0.12	0.26	1.35	0.008	0.010	—	0.031	0.0044	0.03	—	—	
	(7)-4	0.13	0.30	1.25	0.003	—	0.009	0.040	0.0015	—	—	0.35	
Comp. Steels	(7)-5	0.13	0.24	1.33	—	0.040	—	0.031	0.0023	—	—	—	
	(7)-6	0.13	0.27	1.35	—	—	0.043	0.035	0.0031	—	—	0.31	
Chemical Composition(%)													
Steel No.	Cu	Ti+Zr+Hf					Ceq (%)	Producing Conditions					
								CM (%)	TiN up to 0.02μ (%)				
Present Invention	(7)-1	—	0.011					0.359	0	0.006			
	(7)-2	—	0.011					0.359	0	0.008			
	(7)-3	—	0.018					0.358	0	0.013			
	(7)-4	0.28	0.012					0.367	0.126	0.006			
Comp. Steels	(7)-5	—	0.040					0.362	0	0.002			
	(7)-6	0.31	0.043					0.382	0.124	0.002			
Steel No.	Soaking Temp. (°C)	Cooling Rate (°C/mm)	Producing Conditions		Heat Treatment	Plate Thickness (mm)	Yield Point (kg/mm <sup>2</sup> )	Material Properties					
			Heating Temp. for Rolling (°C)	Cooling Rate in Rolling (°C/sec)				Tensile Strength (kg/mm <sup>2</sup> )	Elongation (%)	vE-10 (kg-m)	vTrs (°C)		
(7)-1	1380	1.0	1150	2.1	QT	25	50.8	63.5	26	20.3	-40		
(7)-2	1380	60	1150	1.2	AR	32	30.6	47.0	47	15.8	-15		
(7)-3	1350	60	1150	1.2	AR	32	33.9	50.4	45	17.6	-20		
(7)-4	1380	60	1150	2.1	QT	25	57.5	68.1	24	22.1	-45		
(7)-5	1380	60	1150	2.1	QT	25	51.5	64.3	25	18.6	-25		
(7)-6	1380	60	1150	2.1	QT	25	59.3	69.7	23	19.5	-35		
Steel No.	Maximum Hardness (JISZ 3101)	Welding Properties			Toughness of Large Heat-Input Welded Joint			vEo (kg-m)					
		Toughness of HAZ of Shielded Arc Welding	Welded Joint		Welding Method and Heat Input (KJ/cm)								
(7)-1	327		14.7		EG 150		9.8						
(7)-2	343		18.6		ES 320		12.0						
(7)-3	341		20.3		ES 320		19.5						
(7)-4	331		13.6		EG 150		9.5						
(7)-5	329		9.4		EG 150		1.7						
(7)-6	335		10.8		EG 150		1.9						

What is claimed is:

1. A method for producing steel materials suitable for large heat-input welding, which comprises heating a steel ingot or slab containing 0.03 to 0.18% C, 0.1 to 1.0% Si, 0.5 to 1.8% Mn, not more than 0.1% total Al, 0.004 to 0.03% Ti, and 0.001 to 0.009% total N, with the balance being Fe and unavoidable impurities to a temperature between 1250° and 1400°C so as to dissolve not less than 0.004% of the TiN into solid solution and then reprecipitating the dissolved TiN into fine TiN.
2. The method according to claim 1, in which the reprecipitation of the dissolved TiN is done by working the steel after the heating.
3. The method according to claim 1, in which the reprecipitation of the dissolved TiN is done by reheating the steel to a temperature not higher than 1150°C after the heating.
4. The method according to claim 2, in which the working is rolling or forging.
5. A method for producing steel materials suitable for large heat-input welding, which comprises heating a steel ingot or slab containing 0.03 to 0.18% C, 0.1 to 1.0% Si, 0.5 to 1.8% Mn, not more than 0.1% total Al, 0.004 to 0.03% Ti, and 0.001 to 0.009% total N, with the balance being Fe and unavoidable impurities to a temperature between 1250° and 1400°C so as to dissolve not less than 0.004% of the TiN into solid solution, rolling or forging the steel, forcedly cooling the steel to a temperature not higher than 800°C, and then reheating the steel to a temperature not higher than 11-

50°C so as to reprecipitate the dissolved TiN into fine TiN.

6. A method for producing steel materials suitable for large heat-input welding, which comprises heating a steel ingot or slab containing 0.03 to 0.18% C, 0.1 to 1.0% Si, 0.5 to 1.8% Mn, not more than 0.1% total Al, 0.004 to 0.03% Ti, and 0.001 to 0.009% total N, with the balance being Fe and unavoidable impurities to a temperature between 1250° and 1400°C so as to dissolve not less than 0.004% C of the TiN into solid solution, rolling or forging the steel with a finishing temperature not lower than 1000°C, and reheating the steel at a temperature not higher than 1150°C so as to reprecipitate the dissolved TiN into fine TiN.

7. A method for producing steel materials suitable for large heat-input welding, which comprises heating a steel ingot or slab containing 0.03 to 0.18% C, 1 to 1.0% Si, 0.5 to 1.8% Mn, not more than 0.1% total Al, 0.004 to 0.03% Ti, 0.001 to 0.009% total N, and 0.001 to 0.03% REM with the balance being Fe and unavoidable impurities and satisfying the condition of REM/S = 1.0 to 6.0, to a temperature between 1250° and 1400°C so as to dissolve not less than 0.004% of the TiN into solid solution, and reprecipitating the dissolved TiN into fine TiN.

8. A method for producing steel materials suitable for large heat-input welding according to claim 7 in which the reprecipitation of the dissolved TiN is done by working the steel after the heating.

9. A method for producing steel materials suitable for

large heat-input welding according to claim 7 in which the reprecipitation of the dissolved TiN is done by reheating the steel to a temperature not higher than 1150°C after the heating.

10. A method for producing steel materials suitable for large heat-input welding which comprises heating a steel ingot or slab containing 0.03 to 0.18% C, 0.1 to 1.0% Si, 0.5 to 1.8% Mn, not more than 0.1% total Al, 0.004 to 0.03% Ti, 0.001 to 0.009% total N, one or more of not more than 0.05 Nb, not more than 0.08% V and not more than 0.003% B with the balance being iron and unavoidable impurities to a temperature between 1250° and 1400°C so as to dissolve not less than 0.004% of the TiN into solid solution, and reprecipitating the dissolved TiN into fine TiN.

11. A method for producing steel materials suitable for large heat-input welding according to claim 10 in which the reprecipitation of the dissolved TiN is done by working the steel after the heating.

12. A method for producing steel materials suitable for large heat-input welding according to claim 10 in which the reprecipitation of the dissolved TiN is done by reheating the steel to a temperature not higher than 1150°C after the heating.

13. A method for producing steel materials suitable for large heat-input welding which comprises heating a steel ingot or slab containing 0.03 to 0.18% C, 0.1 to

1.0% Si, 0.5 to 1.8% Mn, not more than 0.1% total Al, 0.004 to 0.03% Ti, 0.001 to 0.009% total N, one or more of not more than 0.35% Cr, not more than 0.35% Mo, not more than 0.6% Cu, not more than 1.5% Ni, and not more than 1.0% W, with the balance being iron and unavoidable impurities and satisfying the condition of  $(\text{Cu}+\text{Ni}+\text{W})/5+\text{Cr}+\text{Mo} \leq 0.75\%$  to a temperature between 1250° and 1400°C, and reprecipitating the dissolved TiN into fine TiN.

14. A method for producing steel materials suitable for large heat-input welding according to claim 13 in which the reprecipitation of the dissolved TiN is done by working the steel after the heating.

15. A method for producing steel materials suitable for large heat-input welding according to claim 13 in which the reprecipitation of the dissolved TiN is done by reheating the steel to a temperature not higher than 1150°C after the heating.

16. A method for producing steel materials suitable for large heat-input welding according to any of the preceding claims in which 0.004 to 0.03% Ti is replaced by the same amount of one or more of Ti, Zr and Hf so as to assure a solid solution of nitrides in an amount of not less than 0.004% as one or more of TiN, ZrN and HfN during the heating step and reprecipitate fine TiN, ZrN or HfN.

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