A metallurgical method for refining grains of steel includes adding aluminum into molten steel obtained from a secondary refining process. Aluminum reacts with oxygen and sulfur in the molten steel to reduce the total oxygen content in the molten steel to 15-120 ppm, to reduce a sulfur content in the molten steel to 15-150 ppm, and to produce aluminum oxide, obtaining cleaner molten steel. Magnesium is added into the cleaner molten steel and reacts with oxygen, sulfur, and aluminum oxide in the cleaner molten steel to reduce the total oxygen content in the molten steel to 10-60 ppm, to reduce the sulfur content in the molten steel to 5-100 ppm, and to produce inclusions including magnesium oxide, magnesium sulfide, and magnesium-aluminum spinel. Precipitates of the inclusions can serve as crystalline cores in a subsequent crystallization process to obtain fine-grained steel.
FIG. 1
PRIOR ART

1. Electric arc furnace step
2. Converter steelmaking step
3. Secondary refining process step
4. Thermo mechanical control process step
5. Alloyization step

S91
S92
S93
S94
FIG. 2

FIG. 3
FIG. 6

FIG. 7
METALLURGICAL METHOD FOR REFINING GRAINS OF STEEL BY MODIFYING INCLUSIONS THROUGH ADDITION OF MAGNESIUM AND ALUMINUM

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] The present invention relates to a metallurgical method and, more particularly, to a metallurgical method for refining grains of steel by modifying inclusions in the molten steel through addition of magnesium and aluminum.

[0003] 2. Description of the Related Art

[0004] Molten steel obtained from convertor steelmaking and electric arc furnaces is generally refined by ladle furnaces (LF), vacuum degassers (VD), recirculating degassers (RfI), vacuum oxygen degassers (VOD), or vacuum arc degassers (VAD) to reduce the content of phosphorus, sulfur, oxygen, nitrogen, and hydrogen. Appropriate adjustment of the content of carbon and alloy is allowable to obtain ideal content ranges to meet requirements of specific properties of steel.

[0005] Conventional steelmaking methods include making steel by using an electric arc furnace S91 or convertor steelmaking S91, and a secondary refining process S92 (see FIG. 1). Decarburization of the molten steel obtained from the electric arc furnace S91 or convertor steelmaking S91 can be carried out by blowing oxygen into the molten steel, generating a gas such as carbon monoxide or carbon dioxide, and the gas is then exhausted. The resultant molten steel includes a higher total oxygen content (including dissolved oxygen and oxygen in oxides) and more inclusions. The quality of the steel will be affected if the molten steel with higher oxygen content is directly continuous casting. The quality of the steel can be significantly improved by the secondary refining process S92 including deoxidization, desulfurization, degassing, lowering carbon, etc. The refined molten steel can be continuous casting and then rolled into steel products.

[0006] High technology industries have strict standards for steel products due to explosive development of current technologies. Thus, in addition to development of ultra clean steel, the performances of the clean steel are enhanced in the expectation of finding steel with higher strength and higher toughness. The development focuses on the properties of the molten steel after the second refining process S92, seeking super steel (particularly steel slab) having a yield strength higher than 1000 Mpu to meet the market demands.

[0007] Currently, the tissue and arrangement of the grains of the steel are improved by grain refining strengthening, solid solution strengthening, precipitation strengthening, and secondary strengthening according to the material refining principles to increase the material strength of the steel. As an example, alloy elements, such as chromium, manganese, nickel, rare earth metal, etc., are added into the molten steel obtained above the secondary refining process S92 in an alloyization process S93 to increase the strength, toughness, and other properties of steel through solid solution strengthening or precipitation strengthening. In another example, the grains of steel can be refined by a thermo mechanical control process (TMCP) S94 that controls the rolling temperature, cooling speed, and rolling speed to obtain fine grains. Finer grains are obtained (the diameters of the grains are about 5-10 μm) to enhance the strength and toughness of steel.

[0008] However, these conventional methods are expensive while providing limited improvement in properties. Taking alloyization as an example, it relies on the expensive alloy elements to enhance the strength of steel, and the improvement of the strength is limited by the properties of the alloy elements per se. The costs are, thus, increased, and the properties of steel are usually enhanced by not more than 20%. Taking TMCP that can produce high strength steel having a yield strength of 700-900 Mpa as another example, during the thermo mechanical control process (TMCP) S94, the conditions for controlling phase change of steel, such as rolling temperature, rolling speed, or cooling speed, must be strictly controlled so as to precisely refine the grains of steel. This requires a vast sum of money to expand the equipment, and the refining procedures are costly, leading to limitation to the development of TMCP.

[0009] Thus, a need exists for a metallurgical method for refining grains of steel obtained from the secondary refining process through interaction between magnesium/aluminum and molten steel to solve the above problems.

SUMMARY OF THE INVENTION

[0010] An objective of the present invention is to provide a metallurgical method for refining grains of steel by modifying the inclusions of the molten steel through addition of magnesium and aluminum. The metallurgical method can directly modify the inclusions of the molten steel obtained from the secondary refining process to increase the cleanliness. At the same time, by using the thermodynamic conditions of the molten steel, the compositions, sizes, forms, and distribution of the inclusions are modified to increase the amount of crystalline cores in steel, enhancing refining of the steel grains and, hence, enhancing the strength and toughness of steel.

[0011] Another objective of the present invention is to provide a metallurgical method for refining grains of molten steel by modifying the inclusions of the molten steel through addition of magnesium and aluminum, reducing the costs of the procedures and improving the properties of steel.

[0012] The present invention fulfills the above objectives by providing a metallurgical method for refining grains of steel obtained from the secondary refining process. The metallurgical method includes a pre-processing step and a modification step. In the pre-processing step, aluminum is added into the molten steel obtained from the secondary refining process. Aluminum reacts with oxygen and sulfur in the molten steel to reduce the total oxygen content in the molten steel to 15-120 ppm, to reduce sulfur content in the molten steel to 15-150 ppm, and to produce aluminum oxide (Al₂O₃), obtaining cleaner molten steel. In the modification step, magnesium is added into the cleaner molten steel. Magnesium reacts with oxygen, sulfur, and aluminum oxide in the cleaner molten steel to reduce the total oxygen content in the molten steel to 10-60 ppm, to reduce the sulfur content in the molten steel to 5-100 ppm, and to produce inclusions. The inclusions include magnesium oxide, magnesium sulfide, and magnesium-aluminum spinel. The magnesium-aluminum spinel has a melting point higher than 2000°C, and the diameters of the grains of the magnesium-aluminum spinel are in a range of 0-3 μm, mostly 1 μm. Magnesium sulfide is in the form of particles and has a high melting point, which is advantageous to clean the grain boundary. The tiny inclusions having high melting points are uniformly distributed in the molten steel. Aggregation and growth of the inclusions are less likely to occur. In subsequent procedure of continuous casting and
rolling of steel, precipitated inclusions can serve as crystal-line cores during a crystallization process of the molten steel, obtaining fine-grained steel.

In the modification step, 0.01-0.6 kilograms of magnesium per ton of cleaner molten steel is added. Furthermore, a magnesium-aluminium alloy wire including 5-80 wt % of magnesium is added into the cleaner molten steel.

Each of the pre-processing step and the modification step is carried out in a temperature range of 1843K to 1903K (1570°C to 1670°C). The molten steel obtained from the secondary refining process is medium carbon steel or low carbon steel.

The present invention will become clearer in light of the following detailed description of illustrative embodiments of this invention described in connection with the drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

The illustrative embodiments may best be described by reference to the accompanying drawings where:

FIG. 1 shows a flow block diagram of a conventional method for refining steel.

FIG. 2 shows a flow block diagram of a method for refining molten steel according to a preferable embodiment of the present invention.

FIG. 3 shows a thermodynamic equilibrium diagram of oxygen and aluminum in the molten steel according to a preferable embodiment of the present invention.

FIG. 4 shows a thermodynamic equilibrium diagram of magnesium/aluminium/Mg—Al spinel and magnesium oxide/aluminium oxide/Mg—Al spinel in the molten steel according to a preferable embodiment of the present invention.

FIG. 5 shows a thermodynamic equilibrium diagram of aluminum and magnesium in the molten steel according to a preferable embodiment of the present invention.

FIG. 6 shows a thermodynamic equilibrium diagram of magnesium/oxygen and magnesium/aluminium oxide in the molten steel according to a preferable embodiment of the present invention.

FIG. 7 shows a phase diagram of the Mg—Al spinel in the molten steel obtained from the method according to a preferable embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

FIG. 2 shows an example of a metallurgical method for refining grains of steel by modifying inclusions through addition of magnesium and aluminium according to a preferable embodiment of the present invention. The metallurgical method according to the preferable embodiment of the present invention includes a pre-processing step S1 and a modification step S2. The metallurgical method according to the preferable embodiment of the present invention is used to refine the molten steel obtained from a secondary refining process. The term “molten steel” used hereinafter refers to the molten steel obtained from the secondary refining process having a higher cleanliness.

In the pre-processing step S1, aluminum is added into the molten steel obtained from the secondary refining process, with aluminum reacting with oxygen and sulfur in the molten steel to reduce the total oxygen content in the molten steel to 15-200 ppm, to reduce sulfur content in the molten steel to 15-150 ppm, and to produce aluminium oxide (Al2O3), obtaining cleaner molten steel. More specifically, due to good deoxidization effect, aluminum is generally used in steelmaking procedures as a deoxidizer to reduce oxygen in the molten steel to a low extent meeting strict standards. According to the thermodynamic equilibrium principle, the oxygen content in the molten steel decreases as the amount of aluminum added into the molten steel is increased, and aluminium reacts with oxygen to produce aluminium oxide (Al2O3) (see Equation (1) below). At the same time, the total oxygen content in the molten steel is preferably in a range of 15-120 ppm. Due to mutual affection between aluminium and sulfur, the sulfur content in the molten steel is approximately in a range of 15-150 ppm, for obtaining the molten steel containing a large amount of aluminium oxide (Al2O3).

\[
2[Al]+3[O] \rightarrow Al_2O_3(s), \Delta G^\circ = -120270+386.28 T
\]

It is noted that \( \Delta G^\circ \) indicates a change of the free energy after chemical reaction in a standard status, and it indicates the activity of each element in the standard status. The equilibrium relationship between [Al] and [O] can be calculated by Equation (1) and the Activity Theory, as shown in the following expression:

Thus, the thermodynamic equilibrium relationship between [Al] and [O] in the molten steel shown in FIG. 3 is obtained.

In an example, reaction of the aluminum in the pre-processing step S1 underwent in a temperature range of 1843K to 1903K, particularly at 1873K. 0.02-2 kilograms of magnesium (based on the total oxygen content in the molten steel) was added into the molten steel, allowing reaction between aluminum and oxygen in the molten steel to produce a large amount of aluminum oxide (Al2O3). Thus, the total oxygen content in the molten steel was reduced to 15-150 ppm, and the sulfur content in the molten steel was reduced to 15-150 ppm, obtaining cleaner molten steel containing extremely small amount of oxygen and sulfur and containing a large amount of aluminum oxide (Al2O3), which is suitable for the subsequent modification step S2.

However, the grains of aluminum oxide (Al2O3) are apt to aggregate to sizes that may block the ladle nozzle by the large amount of aluminum oxide (Al2O3) in the cleaner molten steel, in the subsequent casting procedure of the molten steel. Thus, the modification step S2 must be carried out on the cleaner molten steel.

In the modification step S2, magnesium is added into the cleaner molten steel. Magnesium reacts with oxygen, sulfur, and aluminum oxide in the cleaner molten steel to reduce the total oxygen content in the molten steel to 10-60 ppm, to reduce the sulfur content in the molten steel to 5-100 ppm, and to produce inclusions. The inclusions include magnesium oxide, magnesium sulfide, and magnesium-aluminum spinel. Precipitated inclusions are adapted to serve as crystalline cores in a subsequent crystallization process following the modification step S2, obtaining fine-grained steel in the crystallization process. Specifically, the tiny inclusions having high melting points are uniformly distributed in the molten steel. Aggregation and growth of the non-metallic inclusions are less likely to occur. Thus, the precipitated of the inclusions can serve as crystalline cores of steel in subsequent continuous casting and rolling procedures, enhancing crystallization of steel grains that turn into tiny steel grains.

To assure achievement of the above objectives, thermodynamic analytic calculation was carried out to verify the feasibility.
Magnesium reacted with oxygen and sulfur residing in the cleaner molten steel to produce magnesium oxide and magnesium sulfide (see Equations (2) and (3) below). Mutual transformation between magnesium oxide and magnesium sulfide occurred when the thermodynamic reaction reaches equilibrium (see Equation (4) below). Formation, amount, size, and forms of the inclusions were controlled by thermodynamic conditions to obtain mutual restriction between [Mg]—[O] and [Mg]—[S], maintaining the equilibrium between [Mg], [Al], [O], [S], magnesium oxide, and magnesium sulfide.

$$\Delta G = -RT \ln \left( \frac{[Mg]}{[Mg]_0} \times \frac{[S]}{[S]_0} \right) = -1969070 + 623.87T$$

The following expression can be obtained from Equations (2) and (4):

$$% \text{Mg}: = 2.64 \times 10^{-4} \frac{[Mg]}{[Mg]_0}$$

Equation (5) shows that the reaction in area B was controlled by the thermodynamic equilibrium condition. In a case that [Mg]/[Al] > 2.64 x 10^{-4}, the reaction fell in area B below curve 1, and magnesium-aluminum spinel was formed. On the other hand, if [Mg]/[Al] < 2.64 x 10^{-4}, the reaction fell in area B below curve 1, and magnesium oxide was formed instead. Furthermore, curve 2 represents a critical condition of transformation of aluminum, magnesium, and magnesium-aluminum spinel (corresponding to the right side axis) specifically, after treating the molten steel with magnesium and aluminum, the activity a of each element was substituted into the above free energy equilibrium equation.

$$AG = -1969070 + 623.87T$$

The following expression can be obtained from Equations (2) and (4):

$$\frac{[% \text{Al}]}{[% \text{Mg}]} = 2.64 \times 10^{-4}$$

Equation (5) shows that the reaction in area B was controlled by the thermodynamic equilibrium condition. In a case that [Mg]/[Al] > 2.64 x 10^{-4}, the reaction fell in area B below curve 1, and magnesium-aluminum spinel was formed. On the other hand, if [Mg]/[Al] < 2.64 x 10^{-4}, the reaction fell in area B below curve 1, and magnesium oxide was formed instead. Furthermore, curve 2 represents a critical condition of transformation of aluminum, magnesium, and magnesium-aluminum spinel (corresponding to the right side axis) specifically, after treating the molten steel with magnesium and aluminum, the activity a of each element was substituted into the above free energy equilibrium equation.

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tallization process, enhancing formation of the cores of Acicular Ferrite (AF) in the grains and, hence, enhancing crystallization of steel, refining the grain tissue of steel and improving the strength and toughness of steel.

[0043] In an example, 0.01-0.6 kilograms of magnesium per ton of cleaner molten steel was added at 1873K. Specifically, a magnesium-iron alloy wire including 5-80 wt % of magnesium was added into the cleaner molten steel. Magnesium reacted with oxygen and sulfur to produce magnesium oxygen and magnesium sulfide under mutual restriction according to thermodynamic equilibrium. At the same time, the formed magnesium oxide further reacted with aluminum oxide to produce magnesium-aluminum spinel. Formation of magnesium-aluminum spinel having tiny grains was conditioned according to the thermodynamic equilibrium principle (see FIG. 4) to reduce the total oxygen content in the molten steel to 10-60 ppm and to reduce the sulfur content in the molten steel to 5-100 ppm. Thus, the non-metallic oxides including the above-mentioned magnesium oxide, magnesium sulfide and magnesium-aluminum spinel were distributed in a uniform, non-aggregation, and scattered manner according to the thermodynamic equilibrium principle. The diameters of most of the grains of the non-metallic oxides were smaller than 3 mm. When using the precipitated inclusions as the crystalline cores of the molten steel during crystallization, formation of the cores of Acicular Ferrite (AF) in the grains can be enhanced to refine the grains of steel. Due to large-angle grain boundary between adjacent two pins of the Acicular Ferrite on any one of the crystalline cores in the grains, the grains of steel deflected and were refined while the pattern of the tiny cracks in steel goes across the crystalline cores of the Acicular Ferrite in the grains. The strength and toughness of steel were improved. Thus, it is sufficient to develop steel having yield strength larger than 1000 Mpa.

[0044] Conclusively, the main features of the metallurgical method for refining grains of molten steel by modifying inclusions of the molten steel through addition of magnesium and aluminum according to the preferable embodiment of the present invention directly modifies the inclusions of the molten steel obtained from the secondary refining process to increase the cleanliness of the molten steel. At the same time, the compositions, sizes, forms, and distribution of the inclusions are modified according to the thermodynamic conditions to increase the amount of crystalline cores in the steel, achieving refining of the steel grains and, further, enhancing the strength and toughness of the steel.

[0046] The metallurgical method for refining grains of steel by modifying the inclusions of the molten steel through addition of magnesium and aluminum can reduce the costs of the procedures and improve the properties of the steel.

[0047] Thus since the invention disclosed herein may be embodied in other specific forms without departing from the spirit or general characteristics thereof, some of which forms have been indicated, the embodiments described herein are to be considered in all respects illustrative and not restrictive. The scope of the invention is to be indicated by the appended claims, rather than by the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are intended to be embraced therein.

What is claimed is:

1. A metallurgical method for refining grains of steel obtained from a secondary refining process, with the method comprising:

   a pre-processing step, with the pre-processing step including adding aluminum into the molten steel obtained from the secondary refining process, with aluminum reacting with oxygen and sulfur in the molten steel to reduce a total oxygen content in the molten steel to 15-120 ppm, to reduce a sulfur content in the molten steel to 15-150 ppm, and to produce aluminum oxide, obtaining a cleaner molten steel; and

a modification step, with the modification step including adding magnesium into the cleaner molten steel, with magnesium reacting with oxygen, sulfur, and aluminum oxide in the cleaner molten steel to reduce the total oxygen content in the molten steel to 10-60 ppm, to reduce the sulfur content in the molten steel to 5-100 ppm, and to produce inclusions, with the inclusions including magnesium oxide, magnesium sulfide, and magnesium-aluminum spinel, with precipitated inclusions serving as crystalline cores in a subsequent crystallization process following the modification step, obtaining fine-grained steel in the crystallization process.

2. The metallurgical method as claimed in claim 1, wherein 0.01-0.06 kilograms of magnesium per ton of the cleaner molten steel is added in the modification step.

3. The metallurgical method as claimed in claim 1, wherein a magnesium-iron alloy wire is added into the cleaner molten steel in the modification step, with the magnesium-iron alloy wire including 5-80 wt % of magnesium.

4. The metallurgical method as claimed in claim 1, wherein each of the pre-processing step and the modification step is carried out at 1843K to 1903K.

5. The metallurgical method as claimed in claim 1, wherein the molten steel obtained from the secondary refining process is medium carbon steel or low carbon steel.

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