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(54) METHOD FOR SMELTING HIGH-ALUMINUM-LOW-SILICON ULTRAPURE FERRITIC STAINLESS STEEL

(57) A method for smelting high-aluminum-low-silicon ultrapure ferritic stainless steel is disclosed in the present invention. First, vacuum oxygen decarburization (VOD) and free decarburization treatment for the molten ferritic stainless steel are performed in VOD furnace, then a reduction process of VOD vacuum treatment process is improved, and measures such as preliminary deoxidation, final deoxidation, vacuum breaking, addition of high-density aluminum iron, control of the basicity of slag, followed by wire feeding treatment as well as protective casting in a continuous casting process are taken so as to obtain the high-aluminum-low-silicon ultrapure ferritic stainless steel during the continuous casting treatment, such that acid pickling performance of the ultrapure ferritic stainless steel is improved, the purity of the molten steel and the castable performance in the continuous casting process are further improved, meanwhile the method effectively suppresses the formation of the harmful inclusion of the magnesia aluminum spinel, effectively remove the inclusion of Al_2O_3, suppress oxidation of titanium in titanium-containing steel, and avoid blockage of a tundish nozzle in the continuous casting process.

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to the field of stainless steel smelting, in particular, to a method for smelting ferritic stainless steel, in more particular, to a method for smelting high-aluminum-low-silicon ultrapure ferritic stainless steel.

BACKGROUND ARTS

[0002] Ultrapure ferritic stainless steel is a choicest product of ferritic stainless steel, which generally requires a total carbon and nitrogen content less than 150ppm and a total oxygen content less than 40ppm, with an effectively control of quantity, size and type of inclusions. Ultrapure ferritic stainless steel with no requirement for nickel can also partially substitute austenitic stainless steel so as to save nickel resource.

[0003] Typically, deep decarburization and denitrification treatment with oxygen blowingunder ultra-high vacuum is performed in a vacuum oxygen decarburization (VOD) furnace during the process of smelting ultrapure ferritic stainless steel and the regular procedures carried out in the VOD furnace are:

> 1) Transport the AOD treated molten steel in a steel ladle to the working position for VOD treatment. After temperature measurement and constituent determination, the molten steel identified as qualified can be brought into a vacuum chamber followed by vacuum-pumping and bottom stirring; 2) Oxygenblowing decarburization is started under vacuum by the toplance is carried out with bottom stirring. Whether to stop oxygen blowing or not is determined by furnace atmospheres, and the blowing can be stopped when the $CO+CO_2$ content within the furnace atmospheres is lower than a certain value; 3) Free decarburization is performed under ultra-high vacuum with vigorous stirring; 4) A reduction process is carried out with the addition of ferrosilicon, aluminum, lime and fluorspar for deoxidization and alloying of silicon; 5) Vacuum breaking; and 6) Wire-feeding and soft stirring under atmospheric conditions before casting.

[0004] However, during the process of oxygen blowing decarburization in step 2 described previously, the oxygen blown cannot be utilized completely by said decarburization, as a significant proportion of the oxygen would enter the molten pool and present in form of chromium oxide or dissolved oxygen. Therefore, an additional deoxidization treatment is preformed after the free decarburization described in step 3.

[0005] Silicon and aluminum used herein are common elements for deoxidization. Pure silicon deoxidization technology was first applied by Europe steel companies because deoxidization using aluminum would form a large amount of Al_2O_3 inclusion, which has an adverse effect on most of the steel products. However, the total oxygen content in the steel deoxidized with silicon is very high and the total oxygen content in the ingot slab is over 60 ppm, for example, thereby affecting the performance of the final products.

[0006] With the increasing requirements on ultrapure ferritic stainless steel and the total oxygen content in steel needs to be extremely low, attempts have been made and a silicon-aluminum complex deoxidization process was developed to further reduce the oxygen content in steel. The patents related to the silicon-aluminum complex deoxidization process currently available are as follows:

> Japanese Patent No. JP2002030324(A) discloses a method for producing ridging-resistant ferritic stainless steel with silicon-aluminum complex deoxidization process in which ferrosilicon is first added during the deoxidization process in such a manner that the silicon content in the steel is controlled to 0.20-3.0wt% and the slag basicity (CaO/SiO_2 in the slag) is controlled to 1.2-2.4. The deoxidization is then performed with aluminum in such a manner that the content of Ti and the content of Al satisfy Al/Ti=0.01-0.10. This method can elevate the ratio of equiaxed grain (i.e. the percentage of the equiax grain formed in the whole crystal after solidification. For example, the ratio of equiaxed grain at the center of casting slab is the ratio between the diameter of the central equiaxed zone and the diameter of the casting slab) of molten steel in continuous casting process to 60% and have a good control on the constituent of the inclusion. Moreover, the method can also prevent the tundish nozzle from clogging in casting and maintain the final total content of oxygen in the molten steel at a lower level. However, the slag basicity in said patent is controlled between 1.2 and 2.4, suggesting that the oxygen activity of the slag is still very high and it is hard to reduce the content of oxygen within the molten steel to an extremely low level.

[0007] Chinese patent No. CN101058837, titled smelting method for decarburization and denitrogenation of ultra-pure ferrite stainless steel, discloses a method for smelting ultrapure ferritic stainless steel. The molten steel is decarburized under vacuum prior to the addition of ferrosilicon for deoxidization and then adding aluminum for deep deoxidization under vacuum (vacuum degree ≤ 5 mbar). The deoxidization lasts for 5-10 min before fine adjustment with alloy. This deoxidization procedure allows short time for processing with a good deoxidization effect and has been widely used.

[0008] However, there is no description of the specific method for aluminum adding into molten steel in detail in both JP2002030324(A) and CN101058837. As the density of aluminum block/granule is much lower than that of molten steel, the aluminum material added directly under the VOD condition would contact directly with the slag floating in the upper part of the molten steel, and can give rise to strong exothermic reactions, instead of entering the molten steel pool effectively for deoxidization. For these reasons, a direct addition of aluminum would result in a hard control on the aluminum content in steel after the treatment and can not ensure the effect of precipitation deoxidization.

[0009] Additionally, the deoxidization effect, the subsequent processes and the properties of steel can be affected by the final silicon content and/or aluminum after the silicon-aluminum complex deoxidization process, mainly in the following aspects: 1) if the aluminum content in steel is low, the deoxidization effect is not obvious, i.e. the content of oxygen in the molten steel is high, and if followed by titanium wire feeding there would be a large amount of titanium oxide inclusion formed which can clog the tundish nozzle; 2) the latest studies show that ferritic stainless steel with a high silicon content (generally, higher than 0.3%) exhibits difficulty in a subsequent process of acid pickling, which may affect the surface-finish of the stainless steel. Therefore, in order to further improve the quality of product as well as to ensure a smooth production, a low-silicon-high-aluminum requirement in controlling element contents for deoxidization has become a current trend in deoxidization of various types of ultrapure ferritic stainless steel. In particular, the silicon content in steel should be lower than 0.3% or even lower with a lower limit determined according to other requirements on the steel type, and the aluminum content should be controlled between 0.01 and 0.1 %, which can effectively reduce the total oxygen content and prevent the oxidization of titanium in the subsequent process of titanium alloying.

[0010] With respect to the smelting of low-silicon-high-aluminum ultrapure stainless steel, as described above, the relevant patents and regular methods cannot effectively increase the aluminum content in steel to reach the target range required in the VOD process. If the Al content is increased, without a proper control of the basicity of slag, it is still hard to control the silicon content in steel in an appropriate range. If the process of deoxidization with aluminum in smelting carbon steel is used, i.e. to increase the aluminum content in steel by aluminum wire feeding, the aluminum wire feeding has to be preformed only under a non-vacuum condition after the vacuum process and vacuum breaking as it is too hard for an aluminum wire feeding under vacuum. Although this can indeed increase the aluminum content in steel, the stainless steel molten can no longer be subjected to vigorous stirring after aluminum wire feeding and the Al_2O_3 inclusion generated is hard to grow in a short time and get removed. Moreover, aluminum wire feeding under non-vacuum condition would increase the risk of nitrogen adsorption in molten steel and extend processing time as well. Therefore, it is not a reasonable way to feed aluminum wire under a non-vacuum condition. If blowing of aluminum powder is preformed under vacuum condition, the increase of the aluminum content in steel can be achieved but the vacuum blower is complex and hard to control.

[0011] Therefore, the technical problems in increasing the aluminum content in steel under vacuum and effectively controlling the silicon content have not yet been solved practically with the prior-art technique and regular procedures.

Summary of The Invention

[0012] In order to solve the problems described above, the present invention aims to provide a method for smelting high-aluminum-low-silicon ultrapure ferritic stainless steel. By improving the reduction process during the VOD vacuum treatment with the measures of adding high-density ferroaluminum, controlling the slag basicity, performing wire feeding before protected casting in a continuous casting process, high-aluminum-low-silicon ultrapure ferritic stainless steel can be produced through a process from VOD to continuous casting in smelting. With the method of the invention, the property for acid pickling of ultrapure ferritic stainless steel can be improved and the purity and castability of the molten steel in continuous casting can be further improved. The method of the invention can also provide effective inhibition on the formation of magnesia aluminum spinel and the effective removal of Al_2O_3 inclusion as well as the prevention of titanium in titanium-containing steel from oxidation, avoiding blockage of a tundish nozzle in continuous casting process. To achieve the purposes described above, the following technical strategies are used in the invention:

The present invention provides a method for smelting high-aluminum-low-silicon ultrapure ferritic stainless steel, comprising steps as follows:

(1) The molten ferritic stainless steel is subjected to vacuum oxygen decarburization and free decarburization treatments in a VOD furnace and the contents of major constituents in the molten ferritic stainless steel obtained after treatment should meet: Cr between 10 and 23 mass%, C less than 0.01 mass% and N less than 0.01 mass%;
(2) Preliminary deoxidization: to the molten ferritic stainless steel obtained after treatments in step (1), ferrosilicon and/or aluminum blocks are added for preliminary deoxidization, and then lime and fluorspar are added for slag formation followed by a treatment under high-vacuum with vigorous stirring for 5-10 min;
(3) Final deoxidization: into the molten ferritic stainless steel obtained in step (2) ferroaluminum in which the

aluminum content is 20-60 mass% is added for final deoxidization, followed by adding lime and fluorspar for slag formation, and then the mixture is subjected to moderate stirring under vacuum condition for 2-5 min before vigorous stirring under high vacuum condition for 12-18min;
(4) Vacuum breaking;
(5) The molten ferritic stainless steel is subjected to soft stirring for 8-10 min under atmospheric condition before calcium wire feeding, after which soft stirring for 5-10min is performed;
(6) The soft stirring is continued for another 15-30 min and the molten ferritic stainless steel is subjected to continuous casting under protective atmosphere to finally obtain the high-aluminum-low-silicon ultrapure ferritic stainless steel.

[0013] According to the method for smelting high-aluminum-low-silicon ultrapure ferritic stainless steel provided by the invention, in step (2), the total amount of the ferrosilicon and/or aluminum blocks added is 4-9 kg/t, and the silicon content in the ferrosilicon is 70-80%. The mass of lime added is selected from the larger value from the following two ranges: a mass 4 to 6-fold that of the ferrosilicon added or a mass 2 to 3-fold that of the aluminum blocks added; the mass of fluorspar added is 0.05 to 0.3-fold that of the lime added. After the treatment in step (2), the silicon content in the molten ferritic stainless steel is less than 0.1 mass% and greater than 0 and the oxygen content as required is over 0.01 mass%.

[0014] According to the method for smelting high-aluminum-low-silicon ultrapure ferritic stainless steel provided by the invention, in step (3), the amount of pure aluminum in the ferroaluminum added is 2-6 kg/t, and the mass of lime added is 2 to 3-fold that of pure aluminum within the ferroaluminum added, and the mass of fluorspar added is 0.05 to 0.3-fold that of the lime added. After the treatment in step (3), the silicon content in the molten ferritic stainless steel is less than 0.3 mass% and greater than 0, with the aluminum content in a range of 0.01-0.1 mass% and the oxygen content less than 0.003 mass%.

[0015] According to the method for smelting high-aluminum-low-silicon ultrapure ferritic stainless steel provided by the invention, by calcium wire feeding in step (5) pure calcium wire is fed to the molten ferritic stainless steel, in which the amount of the pure calcium wire added is 0.1-0.3 kg/t. After the treatment in step (5), the calcium content in the molten ferritic stainless steel is 15-30 ppm.

[0016] According to the method for smelting high-aluminum-low-silicon ultrapure ferritic stainless steel provided by the invention, in step (5), after the calcium wire feeding and soft stirring, into the molten ferritic stainless steel is fed titanium wire in which the content of pure titanium wire is 1-3 kg/t.

[0017] According to the method for smelting high-aluminum-low-silicon ultrapure ferritic stainless steel provided by the invention, in the finally obtained high-aluminum-low-silicon ultrapure ferritic stainless steel, the silicon content is less than 0.3 mass% and the aluminum content is 0.01-0.1 mass%.

[0018] According to the method for smelting high-aluminum-low-silicon ultrapure ferritic stainless steel provided by the invention, in step (2), when the upper limit of the silicon content as required in the finally obtained high-aluminum-low-silicon ultrapure ferritic stainless steel is 0.3 mass%, all added is ferrosilicon;
when the upper limit of the silicon content as required in the finally obtained high-aluminum-low-silicon ultrapure ferritic stainless steel is less than or equal to 0.2 mass%, all added are aluminum blocks;
when the upper limit of the silicon content as required in the finally obtained high-aluminum-low-silicon ultrapure ferritic stainless steel is in a range of 0.2-0.3 mass%, ferrosilicon and aluminum blocks are added in which the ratio between ferrosilicon and aluminum blocks is as (the upper limit value of the silicon content in the finally obtained high-aluminum-low-silicon ultrapure ferritic stainless steel minus 0.2%) divided by (0.3% minus the upper limit value of the silicon content in the finally obtained high-aluminum-low-silicon ultrapure ferritic stainless steel).

[0019] According to the method for smelting high-aluminum-low-silicon ultrapure ferritic stainless steel provided by the invention, in step (3), the ferroaluminum is in shape of block or globule with a density of 4.5-6.5g/cm^3 and a diameter of 3-6 cm; after treatment in step (3), the mass ratio between CaO and SiO_2 in slag is higher than 2.8, and the mass ratio between CaO and Al_2O_3 in slag is higher than 1.

[0020] According to the method for smelting high-aluminum-low-silicon ultrapure ferritic stainless steel provided by the invention,
the high vacuum vigorous stirring is performed in the condition with a vacuum pressure controlled at or below 800Pa and the flow rate of argon blown from the bottom of the VOD furnace controlled between 4-8 L/(min=•t);
the moderate stirring is performed in the condition with a vacuum pressure controlled at or below 2000Pa and the flow rate of argon blown from the bottom of the VOD furnace controlled between 1-4 L/(min=•t);
the soft stirring is performed in the condition under atmospheric pressure with the flow rate of argon blown from the bottom of the VOD furnace controlled between 1-5 L/(min•t).

[0021] The beneficial effects of the method for smelting high-aluminum-low-silicon ultrapure ferritic stainless steel provided by the invention are:

1. the VOD smelting can be performed with an effectively improved deoxidization efficiency and an increased aluminum content in the steel, as well as preventing silicon element in slag from flowing back to the molten steel in order to control the silicon content in steel at a relatively low level, such that the smelting of high-aluminum-low-silicon ultrapure ferritic stainless steel can be achieved;
2. Measures are taken for protected casting during the continuous casting process, which can prevent the secondary oxidization of the molten steel with a high aluminum content, and used in combination with calcium treatment it can also prevent a tundish nozzle from clogging; additionally, as the deoxidization effect with aluminum and the target control of the aluminum content have been achieved during the VOD process, the Al_2O_3 inclusion formed can grow fully during vigorous stirring in the VOD process, which is allowed to floated upwards effectively after breaking vacuum, thereby improving the purity of the molten steel;
3. The aluminum within the ferroaluminum with a high density added can enter deep enough into the molten steel and greatly reduce the probability of reacting directly with MgO in slag which generates magnesia aluminum spinel so that the formation of the harmful magnesia aluminum spinel inclusion can be effectively restrained. Additionally, both effective removal of Al_2O_3 inclusion and restraining of the formation of the harmful magnesia aluminum spinel inclusion can avoid the blockage of a tundish nozzle;
4. Due to the increase in the aluminum content, if it is required for a type of steel o be Ti-alloyed, the oxidation of titanium can be greatly inhibited during the process of titanium wire feeding and the yield of titanium can be increased, which also plays an active part in preventing a tundish nozzle from clogging caused by titanium oxide;
5. The method disclosed in the present invention is safe and reliable in performance and strong in operability, which can greatly improve the stability of smelting and product quality as well.

DETAILED DESCRIPTION OF THE INVENTION

[0022] The technical principles of the present invention are described as follows:

1. It is required in the present invention that the target contents of silicon and aluminum used in smelting ultrapure ferritic stainless steel are: silicon less than 0.3 mass%, and aluminum between 0.01-0.1 mass%, with the following purposes:

> The silicon content is required to be less than 0.3% mainly to improve the pickling performance for such stainless steel. If the silicon content is higher than 0.3% it becomes harder in pickling for this steel, thus affecting the finish of the steel. In addition, steel in which the silicon content is within said range can provide an ensured tenacity and improved processability; the aluminum content is controlled between 0.01-0.1 mass% mainly for deoxidization effect. Upon thermodynamic calculation, the content of dissolved oxygen is in a range of 0.002-0.0025% (i.e. 20-25ppm) corresponding to an A1 content of 0.01% for molten ferritic stainless steels with different Cr contents. Due to the inclusion included in the calculation of total oxygen, when the total oxygen in the casting slab is required to be less than 30ppm, the aluminum content involved in the present invention should be higher than 0.01 %; in addition, when the upper limit of the aluminum content is set to be 0.1 %, mainly for some titanium-containing steel types, the content ratio between aluminum and titanium should be greater than 0.15; when the upper limit of the aluminum content is 0.1 %, the titanium content can have an upper limit of 0.7%; however, a aluminum content higher than 0.1 % would be costly, which is unnecessary.

2. Preliminary deoxidization and final deoxidization

[0023] For smelting ferritic stainless steel with the contents of silicon and aluminum within the range described above, preliminary deoxidization is first carried out with ferrosilicon and aluminum blocks prior to the final deoxidization with ferroaluminum in the present invention, as shown in steps (2) and (3). The deoxidization of the invention is performed by adding ferrosilicon, aluminum block and ferroaluminum as described for the following reasons: when only ferroaluminum is added during the whole process of deoxidization, as the cost of ferroaluminum is higher than that of ferrosilicon, the overall cost of the smelting would be increased, besides that it is likely to cause an over carburization; however, when only ferrosilicon and aluminum blocks are added, as aluminum blocks are too light to effectively enter the molten steel, the purpose of increasing the aluminum content in steel cannot be achieved; and if the final deoxidization is performed by adding ferrosilicon, aluminum blocks and ferroaluminum together, as the bonding between aluminum and oxygen is much stronger than that between silicon and oxygen, in the condition that the Cr_2O_3 in slag has been substantially reduced, aluminum would react strongly with SiO_2, leading to a prompt increase in the silicon content in steel, such that the required silicon content of less than 0.3% cannot be achieved at the terminal point. Therefore, a prior preliminary deoxidization with ferrosilicon and a part of aluminum blocks is performed in the present invention, during which as the oxygen content in steel cannot be reduced to a very low level, most of silicon element can react with oxygen based on the thermodynamics formula for silicon-oxygen equilibrium and the silicon content in steel can be kept at a lower level during the process. After the preliminary deoxidization, ferroaluminum is added for final deoxidization. As ferroaluminum has a much higher density than that of pure aluminum blocks, it can be ensured that most part of ferroaluminum can sink into the molten steel after entering the molten pool and the aluminum released from melting can first enter the molten steel to achieve an effective precipitation deoxidization and effectively increase the aluminum content in steel. Of course, part of melted aluminum can directly react with slag but this would not obstruct the rapid increase of the aluminum content in steel.

1) Preliminary deoxidization

[0024] In the preliminary deoxidization described in step (2) of the invention, ferrosilicon with a silicon content of 70-80% and/or aluminum blocks are added for preliminary deoxidization, the total amount of the ferrosilicon and/or aluminum blocks added is 4-9 kg/t. In addition, lime and fluorspar are added for slag formation, in which the mass of lime added is the larger value of 4 to 6-fold that of ferrosilicon added and 2 to 3-fold that of aluminum blocks added, and the mass of fluorspar added is 0.05 to 3-fold that of lime added. Vigorous stirring is performed under high vacuum for 5-10 min, after which the silicon content is required to be less than 0.1 mass% and the oxygen content is required to be higher than 0.01 mass%.

[0025] Prior to such step, the molten steel has just been treated with oxygen decarburization and there would be plenty of dissolved oxygen and chromium oxide in the molten pool. The purpose of adding ferrosilicon and aluminum blocks for preliminary deoxidization is to reduce chromium oxide into chromium using ferrosilicon or aluminum blocks and minimize the reduction of oxygen content in the steel. With its strong reducing capability, aluminum blocks can directly react with Cr_2O_3 in slag, and the reducing capability of silicon is mainly discussed herein with an equation of reduction reaction for silicon:

$$1.5\,[Si]+(Cr_2O_3)=2[Cr]+1.5(SiO_2)$$

[0026] Based on thermodynamic calculation, assuming that the thermodynamic activity of oxides (Cr_2O_3) and (SiO_2) with a standard of the pure substance both equal to 1, it can be calculated that the silicon content should be over 0.6% to promote the forward reaction in the steel with a chromium content of 18%, which means that the density of the ferrosilicon cannot be too high so as to ensure the ferrosilicon to float in top part of the molten steel and react directly with (Cr_2O_3) in slag, and the silicon content in contact with slag in part of the molten steel should be higher than 0.6%. Thus, common used ferrosilicon with a silicon content of 70-80% is selected by the invention, which can meet the demand that the density of the ferrosilicon cannot be too high. Of course, the reducing activity of SiO_2 in slag phase with the melting of lime also promotes the preliminary deoxidization with silicon. Aluminum is also selected by the invention for the preliminary deoxidization mainly for the steel type with lower demand for the target silicon content, which will be further described afterwards. For the amounts of ferrosilicon and aluminum blocks added, as the deoxidizing amounts of ferrosilicon containing 75% silicon and aluminum of the same weight is close to 1, to the steel containing low chromium content and low initial carbon content, relatively lower total amount of ferrosilicon and aluminum blocks would be needed, and in contrast, to the steel containing high chromium content and high initial carbon content, relatively higher total amount of ferrosilicon and aluminum blocks would be needed. Analysis can be made with the following two examples likely arise in production in extreme circumstance to determine the range of the total amount of ferrosilicon and aluminum blocks added. Upon calculation, for smelting of ferritic stainless steel with lower chromium content, for instance, the steel with 11.6% of chromium, for the molten steel containing initial carbon content of 0.3% before entering VOD treatment, decarburization can be achieved with oxygen blowing of 7 Nm^3/t steel under vacuum. According to previous experience, about 30-40% of oxygen would react with chromium in steel to form Cr_2O_3, and about 2.6-3.45kg of pure silicon or 3.5-4.6kg of pure aluminum would be needed, and the lower limit value of the total amount of ferrosilicon and aluminum blocks needed is set as 4 kg/t in the present invention considering the silicon content in the ferrosilicon. However, for smelting of ferritic stainless steel with higher chromium content, for example, the steel with 22.6% of chromium, for the molten steel containing initial carbon content of 0.6% before entering VOD, decarburization can be achieved with oxygen blowing of about 13 Nm^3t steel under vacuum. According to previous experience, about 35-45% of oxygen would react with chromium in steel to form Cr_2O_3, and about 5.6-7.24 kg of pure silicon or 7.5-9.7 kg of pure aluminum would be needed, and the upper limit value of the total amount of ferrosilicon and aluminum blocks needed is set as 9 kg/t in the present invention considering the silicon content in the ferrosilicon. The amount of lime added is determined according to the amount of SiO_2 generated. To satisfied the scope of basicity as required, the mass of lime added is determined as the larger value of 4 to 6-fold that of the ferrosilicon added and 2 to 3-fold that of the aluminum blocks added, which can satisfy the scope wherein the slag basicity can be controlled above 2.8, and the mass ratio between CaO and Al_2O_3 in slag is higher than 1. The main purpose of adding fluorspar is to accelerate the dissolving and melting of lime. The amount of fluorspar added is determined based on how easily in lime dissolving. According to production experience, the amount of fluorspar added is determined as 0.05 to 0.3-fold of the mass of lime added. As the ferrosilicon and aluminum blocks added in step (2) cannot significantly reduce the content of dissolved oxygen in steel and the content of oxygen as required is over 0.01 %, it can be ensured that the silicon content in steel is less than 0.1 % upon reaction. Although the scope of the total amount of ferrosilicon and aluminum blocks added is defined in this step, in practice, the oxygen amount that needs to be removed with ferrosilicon and aluminum blocks should be determined according to the specific distribution proportion of the oxygen blown in decarburization, post combustion, wastage, molten pool intake during the decarburization process involved in smelting. The specific value of the total amount of ferrosilicon and aluminum blocks added can be calculated and is in the scope as defined in the invention as the amount of removed carbon being available, post combustion ratio being calculable from compositions of furnace atmosphere, amount of wastage being calculable based on historical data and the proportion of oxygen entering the molten pool being calculable. The proportion of ferrosilicon and/or aluminum blocks added in step (2) of the invention should also be determined:

a. if the upper limit value of the silicon content (i.e. target silicon content) in the finally obtained high-aluminum-low-silicon ultrapure ferritic stainless steel is 0.3 mass%, all added is ferrosilicon ;
b. if the upper limit value of the silicon content in the finally obtained high-aluminum-low-silicon ultrapure ferritic stainless steel is lower than 0.2 mass% (including 0.2 mass%), all added is aluminum block;
c. if the upper limit value of the silicon content in the finally obtained high-aluminum-low-silicon ultrapure ferritic stainless steel is between 0.2-0.3 mass%, the ratio between the ferrosilicon and aluminum block added is (the upper limit value of the silicon content in the finally obtained high-aluminum-low-silicon ultrapure ferritic stainless steel minus 0.2%) / (0.3% minus the upper limit value of the silicon content in the finally obtained high-aluminum-low-silicon ultrapure ferritic stainless steel);

wherein the upper limit of the silicon content in the finally obtained high-aluminum-low-silicon ultrapure ferritic stainless steel means the value which cannot be exceeded for the silicon content.

[0027] Aluminum is also selected in the invention for the preliminary deoxidization mainly for the kinds of steel with lower demand for the target silicon content. If the target silicon content of only lower than 0.3% is required, the target can be achieved by only adding ferrosilicon and by basicity control. However, if the target silicon content of lower than 0.2% is required, considering that an increase amount of silicon (between about 0.1 % and about 0.2%) can form during the final deoxidization, in this case all added should be aluminum. If the target silicon content has an upper limit value between 0.2 and 0.3 mass%, ferrosilicon and aluminum blocks are planned to be added in the invention with a specific ratio determined by the upper limit value of the target silicon content, which can meet the needs.

2) Final deoxidization

[0028] In the final deoxidization described in step (3) of the invention, ferroaluminum is added for the final deoxidization, wherein the ferroaluminum has an aluminum content of 20-60 mass% and a carbon content lower than 0.1 mass%, with iron and some impurity minor elements for the rest. The amount of pure aluminum added in the ferroaluminum is 2-6 kg/t and lime and fluorspar are additionally added wherein the amount of the lime added is 2 to 3-fold that of pure aluminum within the ferroaluminum and the mass of the fluorspar added is 0.05 to 3-fold that of the lime added. The materials are added before moderate stirring under vacuum for 2-5 min prior to vigorous stirring under high vacuum for 12-18 min. It can be ensured that after the treatment, the silicon content is lower than 0.3 mass% and the aluminum content is 0.01-0.1 mass% and the oxygen content is lower than 0.003 mass%.

[0029] Ferroaluminum with a relatively higher density is chosen as the deoxidizer for the final deoxidization, as discussed above, as after the addition of ferroaluminum the aluminum comprised in which can enter the molten steel pool, rather than reacting in large quantities with the oxide in slag and not entering the molten steel pool substantially, as we saw with pure aluminum, which has been proved in production practice. Choosing the ferroaluminum with a aluminum content of 20-60 mass% is not only for providing a density within the range as required, but also for the consideration that if the aluminum content provided is lower than 20%, the iron content would be too high and result in an exorbitant amount of the ferroaluminum needed as there is a requirement for the amount of pure aluminum added in the invention, which can lead to an increase in carburetion and an excessive reducing in the temperature of the molten pool. The energy released by the reaction involving 1 kg of aluminum can be enough for the heating of about 4 kg of iron from room temperature to 1700°C for the current molten steel upon calculation, thus the final aluminum content in the ferroaluminum is determined to be higher than 20%. The requirement of the ferroaluminum with a aluminum content of lower than 60% is mainly for consideration on density control, as the density of ferroaluminum is required as higher than 4.5 g/cm^3, corresponding to an aluminum content of 60%. The requirement of the ferroaluminum with a carbon content lower than 0.01% is mainly for consideration on carburetion, as the target steel type is ultralow carbon steel and it would be better with lower carburetion after the addition of ferroaluminum under control. In the condition that the ferroaluminum added has a carbon content of 0.1 % and the amount of the ferrolauminum added is 10 kg/t steel, a carburetion of 10ppm for the molten steel is substantially acceptable. Therefore the carbon content in the ferroaluminum should be lower than 0.1%, which is also the range of the carbon content allowing the production with ferroaluminum. The calculation of the amount of the ferroaluminum added is based on the amount of pure aluminum therein. The amount of pure aluminum added in the invention is 2-6 kg/t. The aluminum added is not only for removing the dissolved oxygen in steel but also for further reducing Cr_2O_3 in slag that has not been removed during the preliminary deoxidization, which can consume about 0.5-2.4 kg/t of pure aluminum. The aluminum added can further react with SiO_2 in slag, resulting in a silicon reversion of 0.1%-0.2%, which can consume about 1.4-2.6 kg/t of pure aluminum. In addition, another 0.1-1 kg/t of pure aluminum is needed to satisfy the target final aluminum content of 0.01-0.1%. By adding the upper limit values and lower limit values described above, the range of pure aluminum amount needed can be calculated as 2-6 kg/t, and the amount of ferroaluminum added can be a result of the amount of pure aluminum added divided by the aluminum content therein. The purpose of additionally adding lime is to continually maintain the mass ratio between CaO and Al_2O_3 in slag. As required in the step of the invention, the materials should be first subjected to moderate stirring under vacuum for 2-5 minutes after addition, for the reasons that with a certain strength of stirring in steel, aluminum can be facilitated to enter the molten steel, and on one hand if with too much strength of stirring, the ferroaluminum added would be thrown onto the surface of slag, resulting in aluminum unable to enter the molten steel on the other hand. Therefore, moderate stirring is used herein. The vigorous stirring under high vacuum for 12-18 minutes as required in the step is mainly to ensure sufficient time for Al_2O_3 inclusion to grow, allowing a sufficient floating of the inclusion to be removed during the latter soft stirring under atmospheric condition. In addition, it should be noted that as the aluminum in the ferroaluminum can enter the molten steel sufficiently, its direct entering slag and reducing MgO in slag can be avoided when the deoxidization is progressed to a certain degree, and the forming of the magnesia aluminum spinel can be greatly restrained for magnesia aluminum spinel is a kind of harmful inclusion for stainless steel and can cause product defects. Because the use of ferroaluminum provides control on aluminum and silicon, it can be ensured that the silicon content is lower than 0.3 mass% after the treatments mentioned above with the aluminum content between 0.01 and 0.1 mass% and oxygen content lower than 0.003 mass%.

[0030] The shape and density of the ferroaluminum added in step (3) of the invention is also required as granule or block in shape with a diameter of 3-6 cm and a real density of 4.5-6.5 g/cm^3.

[0031] Being in shape of granule or block is for convenience in production and addition. Having a diameter less than 3 cm, the impact depth of the ferroaluminum from hopper into the molten steel pool may be not enough, and having a size less than 6 cm is mainly for consideration that a size too large is not facilitated for feeding. The density range of 4.5-6.5 g/cm^3 as required is mainly for achieving a 2/3 partial immersion into the molten steel after addition. The density of the ferroaluminum should be higher than 4.5 g/cm^3, as the density of molten steel is 6.9-7.2 g/cm^3, and the upper limit of the density of the ferroaluminum should be 6.5 g/cm^3, as the aluminum content is considered as not lower than 20%.

[0032] It is also required in step (3) of the invention that after the final deoxidization, the basicity of slag, i.e. the mass ratio between CaO and SiO_2 slag, should be controlled higher than 2.8, and the mass ratio between CaO and Al_2O_3 in slag should be higher than 1.

[0033] A slag basicity higher than 2.8 after the final deoxidization as required is mainly for the consideration of the control on activity of SiO_2. According to the ternary diagram of CaO-SiO_2-Al_2O_3 activities, under the basicity condition, the activity coefficient of SiO_2 with a standard of pure substance is about 0.028. Upon thermodynamic calculation, taking smelting of ultrapure ferritic stainless steel with a Cr content of 22.6% as an example, corresponding to the aluminum content of 0.01 % and silicon content of 0.3% in steel, the balance SiO_2 activity in slag is 0.009, and the mole fraction of SiO_2 in slag is further back-calculated as 0.32 under this basicity condition. As the basicity has already been preset as higher than 2.8, the content of SiO_2 is no doubt less than 26%, and generally, the mole fraction of which can be controlled within 0.32 according to the range described above. Thus it can be seen that the basicity within this range can ensure that Al can no longer reduce SiO_2 in slag with the silicon and aluminum contents described above. For steel types with a different Cr content, if the Cr content is lower than 22.6%, as Cr is an element which can reduce the activity of silicon and elevate the activity of aluminum, the activity of silicon in steel would be enhanced and the activity of aluminum in steel would be reduced according to thermodynamic principle of smelting, and thereby Al element cannot further reduce SiO_2 in slag. On the contrary, Al element can reduce SiO_2 in slag. In consideration that there is a few types of steel with a Cr content higher than 22.6%, and the further reduction of SiO_2 in slag by Al can be prevented through regulating the SiO_2 content in slag, and an upper limit of basicity set too high would cause the increase of slag amount, it is finally determined in the invention that the basicity of slag should be higher than 2.8, which is also the minimum requirement for the basicity of slag. There is no upper limit for the basicity of slag as required, mainly for the consideration that with a higher aluminum content, Al_2O_3 in slag would be increased and the basicity of slag would be up-regulated, and in the end the slag would even become calcium aluminum slag with a very low SiO_2 content, i.e. slag with CaO-Al_2O_3 as a major constituent, which is allowable in the invention. It is required in the invention that the mass ratio between CaO and Al_2O_3 should be higher than 1, which is mainly for the conditions that the SiO_2 content in slag is relatively low which is converting into calcium aluminum slag, and a mass ratio between CaO and Al_2O_3 higher than 1 as required can ensure that the slag can absorb Al_2O_3 effectively. For calcium aluminum slag with a mass ratio between

CaO and Al_2O_3 in a range of 1.1-1.4, the slag can absorb inclusion effectively and have a good fluidity. There is also no restraint of the upper limit of the ratio between CaO and Al_2O_3, which is also mainly for conditions of non-calcium aluminum slag, and the Al_2O_3 content is allowed to be within a low range. The control on CaO content in slag has already been done in the setting for the amount of lime added in step (2) and step (3).

3. For step (5)

1) Soft stirring

[0034] The soft stirring prior to the feeding of pure calcium wire can allow the Al_2O_3 inclusion grown under vacuum float into the slag phase. The soft stirring after the feeding of pure calcium wire can promote the calcium aluminate inclusion with a low melting point generated after the calcium feeding to further float into the slag phase.

2) Wire feeding

A) Calcium wire feeding (i.e. a process of calcium treatment)

[0035] The process of calcium treatment, i.e. feeding of pure calcium wire into the molten steel under atmospheric pressure by a wire-feeder, provides 0.1-0.3 kg/t of pure calcium feeding. After the calcium wire feeding, the molten steel is subjected to argon blown from the bottom and gently stirred for 5-10 min under atmospheric pressure. The calcium content in the steel should be controlled between 15 and 30ppm after the treatment.

[0036] As the invention aims at the smelting of high aluminum steel, the amount of aluminum added during the deoxidization is relatively high. Although the removal of formed Al_2O_3 inclusion from the molten steel has been processed by taking various measures and the secondary oxidation has been prevented, there is still risk existing in blockage of a tundish nozzle by Al_2O_3 in practice, for the reason that with a high aluminum content, it is still possible for aluminum to reduce MgO in slag and the magnesia aluminum spinel inclusion formed is hard to remove, which can be the cause of the blockage, together with the remained Al_2O_3 inclusion, raising the risk in blockage of a tundish nozzle. Although the risk has already been reduced to a very low level by taking various measures described by the invention, to ensure the highly stability in producing high aluminum steel, the process of calcium treatment is used in the invention to avoid the formation of blockage of a tundish nozzle. Calcium treatment is mainly for conversing the Al_2O_3 inclusion into $12CaO{\cdot}7Al_2O_3$ inclusion with a low melting point. Generally, the maximum content of Al_2O_3 in steel is 0.01 %, and the amount of calcium needed for conversing this amount of Al_2O_3 into $12CaO{\cdot}7Al_2O_3$ inclusion is 67ppm. Additionally, after the calcium treatment, the dissolved content of calcium element itself is required as 0.09- to 0.15-fold that of aluminum content in general. If the aluminum content is 0.03%, the dissolved calcium content should be about 30ppm, which needs 100ppm (i.e. 0.01%) of pure calcium amount for entering the molten steel. Considering that the recovery ratio of calcium for the process of calcium feeding to high aluminum steel is higher than 30%, the feeding amount of pure calcium is finally determined as 0.1-0.3 kg/t, and the calcium content is finally determined to be controlled within the range of 15-30ppm, which can satisfy the calcium treatment for the range of aluminum content in the invention and achieve the effective conversion of the inclusion. If the final calcium content is higher than 30ppm, there exists risk in eroding of the tundish nozzle.

B) Titanium wire feeding

[0037] For smelting steel types containing titanium, titanium wire can also be fed into the molten ferritic stainless steel. The titanium wire has a pure titanium content of 1-3 kg/t and is titanium alloyed. The amount of pure titanium is calculated as the amount of titanium fed multiplied by the titanium content within the titanium wire.

4. For step (6)

1) Soft stirring for 15-30 min

[0038] The stirring time is sufficient for the inclusion to further float, which further improves the purity of the molten steel.

2) Molten steel should be subjected to continuous casting under protective atmosphere

[0039] The continuous casting under protective atmosphere includes argon protection for ladle gate, argon protection for tundish nozzle and argon protection for upper portion of the tundish, aiming at preventing molten steel from reoxidation. These protections are also needed for smelting of high aluminum steel. As the techniques for continuous casting are mature and realizable, they will not be given too much description herein.

5. For moderate stirring, high vacuum vigorous stirring and soft stirring

[0040] The condition of moderate stirring: vacuum pressure controlled under 2000 Pa and flow rate of argon blown from the bottom of the VOD furnace controlled between 1-4 L/(min=•t);
the condition of the vigorous stirring under high vacuum: vacuum pressure controlled under 800 Pa and flow rate of argon blown from the bottom of the VOD furnace controlled between 4-8 L/(min=•t);
the condition of soft stirring: flow rate of argon blown from the bottom of the VOD furnace controlled between 1-5 L/(min•t) under atmospheric pressure.

[0041] Wherein, the relevant parameters are determined based on production practice. It should be ensured that no vigorous billowing presenting on the surface of slag in moderate stirring under vacuum, no impact on production caused by splashing of molten steel in vigorous stirring under high vacuum and no slag surface being blown away in soft stirring. The related range of the blowing rate from the bottom can be finally determined by exploring in production under the condition described above.

[0042] It should be noted that among units related in the invention, the symbol "t" means molten steel in ton; "L" means liter; "min" means minute; "kg/t" means amount in kilogram added into one ton of molten steel; and "L/(min•t)" means the amount of argon blown into one ton of molten steel per minute.

[0043] While the present invention has been described in detail in relation to representative examples concerning the production of low-silicon-high-aluminum ferritic stainless steel and their efficacy achieved, the described embodiments have been presented by way of examples concerning the production of ultrapure ferritic stainless steel with three grades—409, 443 and 445.

Example 1

[0044] The requirements on the refining equipment VOD furnace in the example were: the equipment allows for treatment of 120 t of molten steel; ultimate vacuum lower than 300 Pa; total argon blowing ability from bottom higher than 60 Nm^3/h; magnesia-calcium bricks used as refractory material for ladle. The grade of steel is 409 and the amount of molten steel used was 116000 kg (i.e. 116 t). The initial constituents in the molten steel prior to VOD smelting were:

> C: 0.3%, Si: 0.25%, Cr: 11.6%, S: 0.010%, N: 0.025%, Mn: 0.56%, P: 0.015%, total O: 0.02%, Ti: 0.01%, Al: 0.001%, and Fe and a minute amount of impurity elements for the rest.

[0045] The initial temperature of the molten steel was 1580°C.

[0046] In this example, the target silicon content was lower than 0.26%, and the aluminum content was about 0.03%. The procedures in detail are described as follows:

1) The molten steel was subjected to oxygen decarburization and free decarburization, wherein the oxygen consumption was 885 Nm^3 and the time for free decarburization was 15 min. After the treatments, the temperature of the molten steel was 1630°C, and the constituents of the molten steel were: C: 0.003%, Si: 0.01%, Cr: 11.1%, S: 0.008%, N: 0.007%, Mn: 0.14%, P: 0.015%, total O: 0.04%, Ti: 0.01%, Al: 0.001%, and Fe and a minute of impurity elements for the rest.
2) Preliminary deoxidization: according to the silicon content in the final production of the high-aluminum-low-silicon ultrapure ferritic stainless steel, the upper limit thereof was set as 0.27%, and 400 kg of ferrosilicon with a silicon content of 77%(i.e. 3.45 kg/t; conversion method: 400 kg / 116 t of the molten steel; within the scope of Example 1, excluding the mass of lime and fluorspar, the same conversion method was used) and 200 kg of aluminum blocks (i.e. 1.71 kg/t), amounting to 600 kg (i.e. 5.16 kg/t) was added for preliminary deoxidization, prior to the addition of 1.6 t of lime and 200 kg of fluorspar for slag formation. After the addition of the materials, the vacuum pressure was controlled below 800 Pa, and the argon blowing from the bottom with a stirring strength of 600 L/min (i.e. 5.17 L/(min=•t); conversion method: 600 (L/min) / 116 t of the molten steel; within the scope of Example 1, the same conversion method was used) for 8 min, allowing the preliminary melting of lime. After the treatment, the silicon content was 0.08% and the oxygen content was 0.015%.
3) Final deoxidization: 650kg of ferroaluminum containing 40% aluminum with a diameter of 5 cm, a density of 5.4 g/cm^3 a carbon content of 0.008% and a pure aluminum content of 260kg (i.e. 2.24 kg/t) were added, before the addition of 600 kg of lime and 50 kg of fluorspar for final deoxidization. After all materials were added, the argon flow rate for bottom stirring was regulated to 150 L/min and moderate stirring was performed for 3 min prior to bottom argon blowing with an argon flow rate of 800 L/min (i.e. 6.90 L/(min•t)) for 15 min. After the treatment, the silicon content was 0.19% and the aluminum content was 0.054% and the oxygen content was 7.8ppm. The main constit-

uents in slag were: CaO 60%, SiO_2 12%, Al_2O_3 17%, and MgO 3%, which was satisfied with the requirement on slag basicity that the mass ratio between CaO and Al_2O_3 should be higher than 1. The temperature after the treatment was 1570°C.

4) Vacuum breaking

5) Soft stirring for 10 min, argon blown from the bottom with a stirring strength of 200 L/min (i.e. 1.72 L/(min•t)). Calcium treatment was then performed by adding 20 kg of pure calcium wire (i.e. 0.17 kg/t) by a wire-feeder before soft stirring for 10 min with a stirring strength of 200 L/min (i.e. 1.72 L/(min•t)) under argon blowing from the bottom. This grade of steel needs titanium alloying by titanium wire feeding and the content of pure titanium in the titanium wire was 150 kg (i.e. 1.38 kg/t), and the final titanium content was 0.1 %.

6) The soft stirring was continued for another 20 min with a stirring strength of 180 L/min (i.e. 1.55 L/(min•t)) under bottom blowing of argon. The continuous casting was carried out under protective atmosphere, including the protection of ladle gate and tundish nozzle with argon blowing. The opening of the tundish nozzle was very stable during the casting process without drastic fluctuation, and the general range of fluctuation was within 3%, indicating that no nozzle clogging nor eroding was presented.

[0047] Finally, the molten steel was cast into ingot slab with its constituents as follows:

C: 0.006%, Si: 0.20%, Cr: 11.7%, S: 0.001%, N: 0.008%, Mn: 0.23%, P: 0.015%, total O: 0.0020%, Ti: 0.09%, Al: 0.044%, and Fe and a minute of impurity elements for the rest.

[0048] There was a little increasing in the silicon content after the vacuum breaking, which can be a result of a small amount of SiO_2 in slag being reduced by aluminum; and there was a little decreasing in the aluminum content, for the reason that the contact between aluminum and oxygen was facilitated with the decreasing of temperature over time and a probable secondary oxidation, resulting in the slight decreasing of its content; as the ferroaluminum added in the deoxidization process contained a certain amount of carbon, the carbon content was increased in a degree as compared with that before the treatment, but was still within the scope of ultrapure. The amount of the magnesia aluminum spinel inclusion in the slab was largely reduced as compared with that in regular protocols. The inclusion mainly were TiN or Ti(CN) inclusions having sizes smaller than 5 μm and globular plastic $CaO-Al_2O_3-SiO_2$ inclusion (partly containing a small amount of MgO) with a size smaller than 10 μm, which brought no harm to the performance of the steel, especially to the performance of the surface of steel.

Example 2

[0049] The requirements on the refining equipment VOD furnace in the example were: the equipment allows for treatment of 120 t of molten steel; ultimate vacuum lower than 300 Pa; total argon blowing ability from bottom higher than 60 Nm^3/h; magnesia-calcium bricks used as refractory material for ladle. The grade of steel was 443 and the amount of molten steel used was 108400 kg (i.e. 108.4 t). The initial constituents in the molten steel prior to VOD smelting were:

C: 0.36%, Si: 0.018%, Cr: 20.8%, S: 0.005%, N: 0.015%, Mn: 0.3%, P: 0.010%, total O: 0.02%, Ti: 0.01%, Al: 0.001%, and Fe and a minute amount of impurity elements for the rest.

[0050] The initial temperature of molten steel was 1600°C.

[0051] In this example, the target silicon content was lower than 0.2%, and the aluminum content was about 0.02%. The procedures in detail are described as follows:

1) The molten steel was subjected to oxygen decarburization and free decarburization, wherein the oxygen consumption was 1266 Nm^3 and the time for free decarburization was 20 min. After the treatments, the temperature of the molten steel was 1670°C, and the constituents of the molten steel were:

C: 0.005%, Si: 0.01%,Cr: 19.7%, S: 0.004%, N: 0.004%, Mn: 0.14%, P: 0.015%, total O: 0.05%, Ti: 0.01 %, Al: 0.001 %, and Fe and a minute of impurity elements for the rest.

2): Preliminary deoxidization: according to the silicon content in the final production of the high-aluminum-low-silicon ultrapure ferritic stainless steel, the upper limit was set as 0.2%, and under this condition, all added were aluminum blocks rather than ferrosilicon to avoid silicon increase. 780 kg of aluminum blocks (i.e. 7.20 kg/t; conversion method: 780 kg / 108.4 t of the molten steel; within the scope of Example 2, excluding the mass of lime and fluorspar, the same conversion method was used) were added for preliminary deoxidization, prior to the addition of 1.6 t of lime and 100 kg of fluorspar for slag formation. After the addition of the materials, the vacuum pressure was controlled below 800 Pa, and the argon blowing from the bottom with a stirring strength of 700 L/min (i.e. 6.46 L/(min=•t); conversion method: 700 (L/min) / 108.4 t of the molten steel; within the scope of Example 2, the same conversion method was used) for 6 min, allowing the preliminary melting of lime. After the treatment, the silicon content was 0.04% and the oxygen content was 0.02%.

3) Final deoxidization: 500kg of ferroaluminum (i.e. 4.61 kg/t) containing 40% aluminum with a diameter of 5 cm, a density of 5.4 g/cm^3 a carbon content of 0.01 % and a pure aluminum content of 200 kg (i.e. 1.85 kg/t) were added, before the addition of 400 kg of lime and 50 kg of fluorspar for final deoxidization. After the materials were added, the argon flow rate for bottom stirring was regulated to 200 L/min (i.e. 1.85 L/(min•t)) and moderate stirring was performed for 4 min prior to bottom argon blowing with an argon flow rate of 800 L/min (i.e. 7.38 L/(min•t)) for 18 min. After the treatment, the silicon content was 0.20% and the aluminum content was 0.018% and the oxygen content was 10ppm. The main constituents in slag were: CaO 55%, SiO_2 2%, Al_2O_3 37%, and MgO 5%, which was satisfied with the requirement on slag basicity that the mass ratio between CaO and Al_2O_3 should be higher than 1. The temperature after the treatment was 1605°C.

4) Vacuum breaking

5) Soft stirring for 9 min, argon blown from the bottom with a stirring strength of 200 L/min (i.e. 1.85 L/(min•t)). Calcium treatment was then performed by adding 12.8 kg of pure calcium wire (i.e. 0.12 kg/t) by a wire-feeder before soft stirring for 10 min with a stirring strength of 200 L/min (i.e. 1.85 L/(min•t)) under argon blowing from the bottom. This grade of steel needs titanium alloying by titanium wire feeding and the content of pure titanium in the titanium wire was 300 kg (i.e. 2.77 kg/t), and the final content of titanium was 0.2%.

6) The soft stirring was continued for another 25 min with a stirring strength of 160 L/min (i.e. 1.48 L/(min•t)) under bottom blowing of argon. The continuous casting was carried out under protective atmosphere, including the protection of ladle gate and tundish nozzle with argon blowing.

[0052] The opening of the tundish nozzle was very stable during the casting process without drastic fluctuation, and the general range of fluctuation was within 3%, indicating that no nozzle clogging nor eroding was presented.

[0053] Finally, the molten steel was cast into ingot slab with its constituents as follows: C: 0.008%, Si: 0.20%, Cr: 20.8%, S: 0.001%, N: 0.006%, Mn: 0.21%, P: 0.015%, total O: 0.0018%, Ti: 0.15%, Al: 0.019%, and Fe and a minute of impurity elements for the rest.

[0054] The aluminum content was slightly increased, which was probably resulting from further declining of oxygen potential of molten steel caused by titanium feeding, but the silicon content remained unchanged, for the reason that the extremely low SiO_2 content in slag can avoid further reduction of silicon in slag by aluminum or titanium during the deoxidization process; since the ferrosilicon added during the deoxidization process contained a certain amount of carbon, the carbon content was increased in a degree as compared with that before the treatment, but was still within the scope of ultrapure.

[0055] The amount of the magnesia aluminum spinel inclusion in the slab was largely reduced as compared with that in regular protocols. The inclusion mainly were TiN or Ti(CN) inclusions having sizes smaller than 5 μm and globular plastic $CaO-Al_2O_3-SiO_2$ inclusion (partly containing a small amount of MgO) with a size smaller than 10 μm, which brought no harm to the performance of the steel, especially to the performance of the surface of steel.

Example 3

[0056] The requirements on the refining equipment VOD furnace in the example were: the equipment allows for treatment of 120 t of molten steel; ultimate vacuum lower than 300 Pa; total argon blowing ability from bottom higher than 60 Nm^3/h; magnesia-calcium bricks used as refractory material for ladle. The grade of steel was 444 and the amount of molten steel used was 110000 kg (i.e. 110 t). The initial constituents in the molten steel prior to VOD smelting were:

C: 0.40 %, Si: 0.06%, Cr: 18.8%, S: 0.005%, N: 0.012%, Mn: 0.3%, P: 0.010%, total O: 0.02%, Ti: 0.01%, Al: 0.001%, and Fe and a minute amount of impurity elements for the rest. The initial temperature of molten steel was 1620°C.

[0057] In this example, the target silicon content was lower than 0.3%, and the aluminum content was about 0.04%. The procedures in detail are described as follows:

1) The molten steel was subjected to oxygen decarburization and free decarburization, wherein the oxygen consumption was 1440 Nm^3 and the time for free decarburization was 20 min. After the treatments, the temperature of the molten steel was 1700°C, and the constituents of the molten steel were:

C: 0.006%, Si: 0.20%, Cr: 17.4%, S: 0.005%, N: 0.005%, Mn: 0.14%, P: 0.015%, total O: 0.05%, Ti: 0.01 %, Al: 0.001 %, and Fe and a minute of impurity elements for the rest.

2) Preliminary deoxidization: according to the silicon content in the final production of the high-aluminum-low-silicon ultrapure ferritic stainless steel, the upper limit was set as 0.3%, and under this condition, all added was ferrosilicon rather than aluminum blocks. 900 kg of ferrosilicon with a silicon content of 77% (i.e. 8.12 kg/t; conversion method: 900 kg / 110 t of the molten steel; within the scope of Example 3, excluding the mass of lime and fluorspar, the same conversion method was used) was added without aluminum blocks for preliminary deoxidization, prior to the addition of 3.6 t of lime and 200 kg of fluorspar for slag formation. After the addition of the materials, the vacuum pressure was controlled below 400 Pa, and the argon blowing from the bottom with a stirring strength of 800 L/min (i.e. 7.27 L/(min=•t); conversion method: 800 (L/min) / 110 t of the molten steel; within the scope of Example 3, the same conversion method was used) for 10 min, allowing the preliminary melting of lime. After the treatment, the silicon content was 0.1 % and the oxygen content was 0.013%.

3) Final deoxidization: 750 kg of ferroaluminum (i.e. 6.82 kg/t) containing 47% aluminum with a diameter of 5 cm, a density of 5.1 g/cm^3 a carbon content of 0.007% and a pure aluminum content of 350 kg (i.e. 3.18 kg/t) were added, before the addition of 700 kg of lime and 200 kg of fluorspar for final deoxidization. After the materials were added, the argon flow rate for bottom stirring was regulated to 200 L/min (i.e. 1.82 L/(min•t)) and moderate stirring was performed for 5 min prior to bottom argon blowing with an argon flow rate of 750 L/min (i.e. 6.82 L/(min•t)) for 18 min. After the treatment, the silicon content was 0.27% and the aluminum content was 0.035% and the oxygen content was 10ppm. The main constituents in slag were: CaO 65%, SiO_2 18%, Al_2O_3 10%, and MgO 5%, which is satisfied with the requirement on slag basicity that the mass ratio between CaO and Al_2O_3 should be higher than 1. The temperature after the treatment was 1642°C.

4) Vacuum breaking

5) soft stirring for 10 min, argon blown from the bottom with a stirring strength of 200 L/min (i.e. 1.82 L/(min•t)). Calcium treatment was then performed by adding 25 kg of pure calcium wire (i.e. 0.23 kg/t) by a wire-feeder before soft stirring for 10 min with a stirring strength of 180 L/min (i.e. 1.64 L/(min•t)) under argon blowing from the bottom. This grade of steel goes without titanium alloying, and there is no need for titanium wire feeding.

6) The soft stirring was continued for another 15 min with a stirring strength of 180 L/min (i.e. 1.64 L/(min•t)) under bottom blowing of argon. The continuous casting was carried out under protective atmosphere, including the protection of ladle gate and tundish nozzle with argon blowing.

[0058] The opening of the tundish nozzle was very stable during the casting process without drastic fluctuation, and the general range of fluctuation was within 5%, indicating that no nozzle clogging nor eroding was presented. Finally, the molten steel was cast into ingot slab with its constituents as follows:

C: 0.01%, Si: 0.29%, Cr: 18.6%, S: 0.001%, N: 0.007%, Mn: 0.21%, P: 0.015%, total O: 0.0017%, Ti: <0.01%, Al: 0.030%, and Fe and a minute of impurity elements for the rest.

[0059] The aluminum content was slightly decreased and the silicon content was remained the same or slightly increased, for the reason that the content of SiO_2 within slag was relatively higher, causing further reduction of silicon in slag by aluminum; and since the ferroaluminum added in the deoxidization process contained a certain amount of carbon, the carbon content was increased in a degree as compared with that before the treatment, but was still within the scope of ultrapure.

[0060] The amount of the magnesia aluminum spinel inclusion in the slab was largely reduced as compared with that in regular protocols. The inclusion mainly were TiN or Ti(CN) inclusions having sizes smaller than 5 μm and globular plastic CaO-Al_2O_3-SiO_2 inclusion (partly containing a small amount of MgO) with a size smaller than 10 μm, which brought no harm to the performance of the steel, especially to the performance of the surface of steel.

[0061] The method for smelting high-aluminum-low-silicon ultrapure ferritic stainless steel provided by the present invention can be used for smelting of low-silicon-high-aluminum ultrapure ferritic stainless steel with a silicon content less than 0.3% and an aluminum content in a range of 0.01-0.1%, and the total oxygen content in the slab is lower than 30ppm, which improves acid pickling property of the product. The method can also restrain the formation of harmful inclusion of the magnesia aluminum spinel and effectively remove the Al_2O_3 inclusion, and restrain the oxidation of titanium in titanium-containing steel, and avoid blockage of a tundish nozzle in continuous casting process.

Claims

1. A method for smelting high-aluminum-low-silicon ultrapure ferritic stainless steel, wherein the method comprises the steps of:

(1) vacuum oxygen decarburization and free decarburization of molten ferritic stainless steel in a vacuum oxygen

decarburization (VOD) furnace, providing molten ferritic stainless steel with the following requirements on constituents: chromium 10-23 mass%, carbon less than 0.01 mass% and nitrogen less than 0.01 %;
(2) preliminary deoxidization: adding ferrosilicon and/or aluminum blocks into the molten ferritic stainless steel obtained in step (1) for preliminary deoxidization with the addition of lime and fluorspar for slag forming, and vigorous stirring under high vacuum for 5-10 min;
(3) final deoxidization: adding ferroaluminum with an aluminum content of 20-60 mass% into the molten ferritic stainless steel obtained in step (2) for final deoxidization with the addition of lime and fluorspar for slag forming before moderate stirring under vacuum for 2-5 min, and then vigorous stirring under high vacuum for 12-18 min;
(4) vacuum breaking;
(5) soft stirring of the molten ferritic stainless steel under atmospheric pressure for 8-10 min before calcium wire feeding to said molten ferritic stainless steel under atmospheric pressure, followed by soft stirring for 5-10 min from the end of said feeding;
(6) soft stirring for another 15-30 min before continuous casting for the molten ferritic stainless steel in protective atmosphere to obtain high-aluminum-low-silicon ultrapure ferritic stainless steel.

2. A method of claim 1, wherein in step (2), the total amount of the ferrosilicon and/or aluminum blocks added is 4-9 kg/t wherein the ferrosilicon has a silicon content of 70-80 mass%, and the mass of the lime added is the larger value between 4- to 6-fold that of the ferrosilicon added or 2- to 3-fold that of the aluminum blocks added; the mass of the fluorspar added is 0.05- to 0.3-fold that of the lime added, and the molten ferritic stainless steel obtained in step (2) is required to have a silicon content lower than 0.1 mass% but higher than 0, and the oxygen content should be higher than 0.01 mass%.

3. A method of claim 1, wherein in step (3), the amount of pure aluminum in the ferroaluminum added is 2-6 kg/t, with the amount of the lime added being 2- to 3-fold that of the pure aluminum in the ferroaluminum added and the amount of fluorspar being 0.05- to 0.3-fold that of the lime added; the molten ferritic stainless steel obtained in step (3) is required to have an silicon content lower than 0.3 mass% but higher than 0, with an aluminum content of 0.01-0.1 mass% and an oxygen content lower than 0.003%.

4. A method of claim 1, wherein in step (5), pure calcium wires are fed to the ferritic stainless steel for the calcium wire feeding with a feed quantity of 0.1-0.3 kg/t; the calcium content in the molten ferritic stainless steel obtained in step (5) is 15-30ppm.

5. A method of claim 1 for smelting high-aluminum-low-silicon ultrapure ferritic stainless steel, wherein in step (5), titanium wires with pure titanium content of 1-3 kg/t are fed to the ferritic stainless steel after the calcium wire feeding and soft stirring.

6. A method of claim 1, wherein the finally obtained high-aluminum-low-silicon ultrapure ferritic stainless steel has a silicon content of lower than 0.3 mass% and an aluminum content of 0.01-0.1 mass%.

7. A method of claim 1 or 2, wherein in step (2),
when the upper limit value of the silicon content in the finally obtained high-aluminum-low-silicon ultrapure ferritic stainless steel is 0.3 mass%, all added is a ferrosilicon;
when the upper limit value of the silicon content in the finally obtained high-aluminum-low-silicon ultrapure ferritic stainless steel is lower than or equal to 0.2 mass%, all added are aluminum blocks;
when the upper limit value of the silicon content in the finally obtained high-aluminum-low-silicon ultrapure ferritic stainless steel is in between 0.2-0.3 mass%, added are ferrosilicon and aluminum blocks; the ratio between the ferrosilicon and aluminum blocks added is (the upper limit value of the silicon content in the finally obtained high-aluminum-low-silicon ultrapure ferritic stainless steel - 0.2%) / (0.3% - the upper limit value of the silicon content in the finally obtained high-aluminum-low-silicon ultrapure ferritic stainless steel).

8. A method of claim 1 or 3, wherein in step (3), the ferroaluminum is in the shape of block or globule with a density of 4.5-6.5 g/cm^3 and a diameter of 3-6 cm; the mass ratio between CaO and SiO_2 is higher than 2.8 and the mass ratio between CaO and Al_2O_3 is higher than 1 in the slag after the treatments in step (3).

9. A method of claim 1, wherein,
the condition of the vigorous stirring under high vacuum: vacuum pressure controlled below 800 Pa and flow rate of argon blown from the bottom of the VOD furnace controlled between 4-8 L/(min=•t);
the condition of moderate stirring: vacuum pressure controlled below 2000 Pa and flow rate of argon blown from

the bottom of the VOD furnace controlled between 1-4 L/(min=•t);
the condition of soft stirring: flow rate of argon blown from the bottom of the VOD furnace controlled between 1-5 L/(min•t) under atmospheric pressure.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2012/070096

A. CLASSIFICATION OF SUBJECT MATTER

See the extra sheet

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: C21C 7/-

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, EPODOC, CNKI, CN-PAT: vacuum, super low carbon, ferritic, ferrite, stainless, refin+, si, silicon, al, alumin?um

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CN 101768656 A (BAOSHAN IRON & STEEL CO., LTD) 07 Jul. 2010 (07.07.2010) fig.1, claims 1, 3, 4, 5, description, embodiments 1, and 3	1-9
A	CN 101058837 A (SHANXI TAIGANG STAINLESS STEEL CO., LT) 24 Oct. 2007 (24.10.2007) see the whole document	1-9
A	CN 101896298 A (POSCO)24 Nov.2010 (24.11.2010) see the whole document	1-9
Y	CN 102199684 A (BAOSHAN IRON & STEEL CO., LTD) 28 Sep. 2011 (28.09.2011) description, embodiment 1 and paragraph [0041]	1-9
Y	CN 102199688 A (BAOSHAN IRON & STEEL CO., LTD) 28 Sep. 2011 (28.09.2011) embodiments 1-3	1-9
A	JP 2008274329 A (KAWASAKI STEEL CORPORATION) 13 Nov. 2008 (13.11.2008) see the whole document	1-9

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&"document member of the same patent family

Date of the actual completion of the international search 05 Jul. 2012 (05.07.2012)	Date of mailing of the international search report 26 Jul. 2012 (26.07.2012)
Name and mailing address of the ISA State Intellectual Property Office of the P. R. China No. 6, Xitucheng Road, Jimenqiao Haidian District, Beijing 100088, China Facsimile No. (86-10)62019451	Authorized officer WANG, Yu Telephone No. (86-10)62084745

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2012/070096

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 9287016 A (NIPPON STEEL CORPORATION)04 Nov.1997 (04.11.1997) see the whole document	1-9
A	JP 57063620 A (SUMITOMO METAL IND LTD) 17Apr.1982 (17.04.1982) see the whole document	1-9

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2012/070096

Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
CN 101768656A	07.07.2010	CN 101768656B	24.08.2011
CN 101058837A	24.10.2007	CN 100557038C	04.11.2009
CN 101896298A	24.11.2010	WO 2009075464A1	18.06.2009
		KR 20090062189A	17.06.2009
		KR 100922061B1	16.10.2009
		US 2011041653A1	24.02.2011
		JP 2011516720A	26.05.2011
CN 102199684A	28.09.2011	None	
CN 102199688A	28.09.2011	None	
JP 2008274329A	13.11.2008	None	
JP 57063620A	17.04.1982	JP 61059367B	16.12.1986
		JP 1392002C	23.07.1987
JP 9287016A	04.11.1997	None	

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2012/070096

Continuation of second sheet **A. CLASSIFICATION OF SUBJECT MATTER**

C21C 7/10 (2006.01) i

C21C 7/06 (2006.01) i

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 2002030324 A **[0006] [0008]**
- CN 101058837 **[0007] [0008]**