Control of Inclusion Composition in Calcium Treated Aluminum Killed Steels

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Inclusions in slab samples with various total calcium, oxygen and sulfur content were investigated in low carbon aluminum killed steel (LCAK steel) with low sulfur content based on industrial experiments and the relationship between steel and inclusions was studied by analyzing inclusions characteristic being detected by SEM-EDS. It is found that T.Ca/T.O could better replace dissolved Ca to evaluate the extent of modification of alumina inclusions by Ca. Inclusions changed from Al_2O_3 based inclusions to Al_2O_3 -CaS inclusions and finally to CaO-CaS inclusions with the increase of T.Ca/T.O in steel for slab samples and MgO and Al_2O_3 content in inclusions almost linearly decreased with T.Ca/T.O in steel. Increasing T.Ca/S in steel could improve the modification extent of alumina by Ca further increased CaS content of inclusions for slab samples with Al_2O_3 -CaS inclusions. In addition, the formation mechanism of inclusions including Al_2O_3 based inclusions, Al_2O_3 -CaS inclusions and CaO-CaS inclusions was discussed.

KEY WORDS: inclusions; composition; calcium treatment; aluminum killed steel.

1. Introduction

For low carbon aluminum killed steel, lots of Al_2O_3 inclusions are generated after aluminum alloy being fed into molten steel with a small amount of dissolved oxygen and they are often considered to be harmful to castability and final product quality. Calcium treatment, by wire feeding, is commonly used to modify solid alumina inclusions to form various typed calcium aluminates. Excess or insufficient calcium addition can produce solid CaS or low modified calcium aluminates with higher melting, which are harmful. In actual production, it is almost impossible to modify all the alumina inclusions to fully liquid ones. Thus, the composition of inclusions, such as MgO, Al_2O_3 , CaO and CaS, should be well controlled in order to get desired properties of steel.

To better control the composition of inclusions, lots of work has been done by previous researchers based on laboratory experiment or thermodynamic calculation. Yang *et al.*^{1,2)} studied the effect of calcium addition on the variation of inclusion composition in low carbon Al-killed steel with induction vacuum furnace and found that the Al_2O_3 content in inclusions linearly decreased by increasing T.Ca/T.O in steel and it disappeared when T.Ca/T.O exceeded 3 and CaS/CaO of the inclusions linearly increased by increasing S/T.O in steel. Numata *et al.*^{3,4)} investigated the calcium consumption and calcium addition pattern on the change of inclusion composition. They found CaO-CaS typed inclusions in steel with 0.0015% sulfur content after calcium

addition. Choudhary *et al.*⁵⁾ developed a thermodynamic model for predicting the formation of oxide-sulfide duplex inclusions in Al-killed steel and found that increasing S content in steel made complete modification of alumina inclusions into liquid calcium aluminate become difficult. Holappa *et al.*⁶⁾ studied the formation and transformation of liquid and solid inclusions containing oxidic and sulphidic components by thermodynamic calculations and found increasing dissolved oxygen content and decreasing sulfur content in steel made the modification of alumina by Ca become easier. Suito *et al.*⁷⁾ calculated the relation among the compositions of inclusion, various typed steel and top slag at 1 823 K based on thermodynamic calculation and found that the contents of Si, O, and Ca in an ultra-low carbon steel were determined as a function of top slag composition. It is worth noting that laboratory experiments only represent for the results of laboratory condition, which often exists difference with the ones of actual conditions, and thermodynamic model also only represent for result of the equilibrium condition, not actual condition.

In present work, inclusions in slab samples with various compositions of molten steel were investigated in Al-killed steel with low sulfur content based on industrial trails. Contents of MgO, Al_2O_3 , CaO and CaS are easily achieved by SEM-EDS and the relation between the compositions of inclusions and molten steel was studied and the formation mechanism of inclusions including Al_2O_3 based inclusions, Al_2O_3 -CaS inclusions and CaO-CaS inclusions was discussed.

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2. Experimental Methods

38 heats industrial trials were carried out in Qian'an Steel Corporation with two kinds of desulfurization method during LF refining to investigate the relation between the compositions of inclusions and molten steel.

The process was as follow, hot metal pretreatment → basic oxygen furnace (BOF) → ladle furnace (LF) → RH → continuous casting (CC) → hot rolling. During the experiment, the steel making process was carried out in a 210 t basic oxygen furnace. After tapping into a ladle, the steel was deslagged, and then a new synthetic slag was added, as well as deoxidizer and the remaining alloys. When the molten steel had the right temperature and chemical composition, the ladle was transferred to the ladle furnace station and alloy was added to deoxidize and meet the composition requirement. During LF refining, the first 28 heats named No. 1 to 28 were desulfurized with the higher basic and stronger reducing refining slag and the remained 8 heats named No. 29 to 36 with relatively lower basicity to achieve higher sulfur content. After LF refining, the ladle was transferred to RH for degassing and removing non-metallic inclusions. After 30 mins RH treatment, various amounts of Ca wire were fed into liquid steel with a speed of 14.4 kg/min and then soft bottom blowing by argon gas was carried out with the flow rate of 10 NL/min for 10 mins. Finally, the slabs with thickness of 230 mm were produced by continuous casting and hot rolled into plate with thickness of 20 mm.

Slag samples were collected from ladles just at the end of RH refining and slab samples (25 mm×25 mm×20 mm thickness), 50 mm from the intrados of slab and plate samples (20 mm×20 mm×20 mm thickness) were also cut from slabs. These metallographic samples were polished by SiC paper and diamond suspensions to characterize the inclusions. The chemical compositions of the steel samples and slag samples were analyzed with chemical methods. Inclusions were observed by scanning electron microscopy (SEM) and ASPEX[®], whose compositions were evaluated by energy dispersive spectrometry (EDS).

3. Experimental Results

3.1. Compositions of Slab and Slag

The compositions of refining slags at the end of RH refining are listed in **Table 1**. By adding synthetic slag and aluminum to the slag, the content of TFe (total Fe) in slag was decreased to <0.8% for No. 1 to 28 and <1.5% for No. 29 to 36 respectively. At the same time, the slag basicity was increased to 6–9 for No. 1 to 28 and 4–7 for No. 29 to 36 respectively, which was benefit for deep desulfurization of the molten steel and ensured the stable subsequent calcium treatment. The composition of slab samples is listed in **Table 2**. Contents of sulfur (S), total aluminum (Alt), total

calcium (T.Ca) and total oxygen (T.O) are in the range of 0.0006–0.0060%, 0.0280–0.0422%, 0.0002–0.0030% and 0.0009–0.0023%.

3.2. Characterization of Inclusions

The element mappings of four kinds of typical inclusions including Al₂O₃ based inclusion, CaO–Al₂O₃ inclusion, Al₂O₃–CaS inclusion and CaO–CaS inclusion detected

Table 2. The composition of 38 heats in slab samples, mass%.

No.	S	Alt	T.Ca	T.O
1	0.0011	0.0281	0.0022	0.0014
2	0.0012	0.0301	0.0024	0.0013
3	0.0009	0.0413	0.0015	0.0008
4	0.0009	0.0420	0.0016	0.0011
5	0.0010	0.0372	0.0015	0.0009
6	0.0011	0.0354	0.0015	0.0010
7	0.0010	0.0358	0.0017	0.0012
8	0.0011	0.0365	0.0017	0.0008
9	0.0007	0.0403	0.0018	0.0009
10	0.0008	0.0418	0.0018	0.0010
11	0.0010	0.0319	0.0012	0.0013
12	0.0010	0.0304	0.0012	0.0014
13	0.0009	0.0381	0.0009	0.0008
14	0.0007	0.0366	0.0005	0.0007
15	0.0008	0.0357	0.0013	0.0009
16	0.0008	0.0346	0.0011	0.0012
17	0.0012	0.0308	0.0005	0.0014
18	0.0011	0.0290	0.0006	0.0013
19	0.0012	0.0335	0.0008	0.0010
20	0.0012	0.0326	0.0008	0.0009
21	0.0008	0.0367	0.0002	0.0013
22	0.0009	0.0350	0.0011	0.0016
23	0.0006	0.0364	0.0013	0.0011
24	0.0007	0.0389	0.0020	0.0015
25	0.0007	0.0305	0.0015	0.0010
26	0.0009	0.0326	0.0008	0.0011
27	0.0009	0.0292	0.0003	0.0009
28	0.0009	0.0344	0.0007	0.0012
29	0.0060	0.0292	0.0023	0.0024
30	0.0030	0.0354	0.0021	0.0020
31	0.0027	0.0393	0.0028	0.0023
32	0.0016	0.0427	0.0014	0.0012
33	0.0040	0.0289	0.0002	0.0015
34	0.0030	0.0291	0.0022	0.0016
35	0.0020	0.0400	0.0023	0.0019
36	0.0021	0.0312	0.0030	0.0018

Total oxygen was analyzed by the inert gas fusion impulse infrared absorption spectroscopy method. Other chemical compositions were obtained by ICP-AES.

Table 1. The composition of refining slag.

process	sample number	CaO mass%	SiO ₂ mass%	Al ₂ O ₃ mass%	TFe mass%	Basicity
1	1–28	50–56	6–10	21–30	<0.8	6–9
2	29–36	40–46	7–12	22–31	<1.5	4–7

in slab samples are shown in **Fig. 1**. Figure 1(a) shows a typical Al_2O_3 based inclusion (or low modified $\text{CaO-Al}_2\text{O}_3$ inclusion), where Al and O distributed almost over the whole inclusion and some of them contained a small amount of calcium. This one could be detected in samples 17–18, 21, 27 and 33. Figures 1(b) and 1(c) show two types of $\text{Al}_2\text{O}_3\text{-CaS}$ complex inclusion, one type of inclusion like inclusion (b) existed a crescent shaped CaS layer surrounding calcium aluminates where Al and Ca uniformly distributed over the whole inclusion and the other type of inclusion like inclusion (c) with an oval CaS layer seemed to be composed of two particles and their formation mechanism has been reported by previous article.⁸⁾ They could be detected in samples No. 11–16, 19–20, 23–24, 26, 28–32 and 34–36. Figure 1(d) shows a typical better modified calcium aluminate, where Ca and Al distributed almost over the whole inclusions and it could be detected in sample 22. Figure 1(e) shows a typical CaO-CaS inclusion, where Ca, S and O distributed almost over the whole inclusion and nearly no aluminum was detected.

3.3. Composition of Inclusions

A large number of inclusions in slab samples were observed by SEM-EDS and ASPEX[®] and the results from EDS show that the component of inclusions mainly contained CaO , Al_2O_3 , CaS and MgO . The average composition of inclusions and number density of all the slab samples are given and shown in **Table 3**, where CC, CA, A and AC mean CaO-CaS inclusion, $\text{CaO-Al}_2\text{O}_3$ inclusion, alumina and $\text{Al}_2\text{O}_3\text{-CaS}$ inclusion respectively. One thing to note is that all inclusions compositions are normalized to unity and other components excluding MgO , Al_2O_3 , CaO and CaS are ignored, which is not of any interest to study alumina inclusions modification.

To better show the composition distribution of inclusions, inclusions with all sizes were projected in $\text{Al}_2\text{O}_3\text{-MgO-CaO}$

or $\text{Al}_2\text{O}_3\text{-CaS-CaO}$ ternary phase diagram mainly based on inclusions components. Three typical types of inclusions from samples No. 1, 13 and 27 were chosen and their compositions were projected in ternary phase diagram shown in **Fig. 2**, where each solid circle represents for an individual inclusion and the solid line for liquidus line in 1 873 K (1 600°C). As can be seen in Fig. 2(a), almost all the points are close to CaO-CaS line in $\text{Al}_2\text{O}_3\text{-CaS-CaO}$ ternary phase diagram and the element mapping of a typical CaO-CaS inclusion is shown in Fig. 1(e). In contrast, the points shown in Fig. 2(b) are mainly close to $\text{Al}_2\text{O}_3\text{-CaS}$ line and part of them contains less CaO content. The elemental mappings of two types of $\text{Al}_2\text{O}_3\text{-CaS}$ inclusions are shown in Figs. 1(b) and 1(c). Besides, the points shown in Fig. 2(c) are close to Al_2O_3 corner, which indicates Al_2O_3 based inclusion is not almost modified by Ca and part of them are modified into $\text{MgO-Al}_2\text{O}_3$ inclusions.

4. Discussion

4.1. Evaluation of Dissolved Ca in Molten Steel

To evaluate the extent of modification of alumina inclusion, Ca content is an important parameter, which includes dissolved Ca in molten steel and undissolved Ca in CaS and CaO , as expressed by Eq. (1). In fact, it is that the dissolved Ca plays an important role in alumina modification. However, dissolved Ca is very difficult to be directly measured accurately. To better evaluate the extent of modification of alumina inclusion by dissolved Ca in steel, the mass ratio of T.Ca/T.O was introduced. The T.O in Table 2 includes dissolved oxygen in steel and undissolved oxygen in oxide inclusions, as expressed by Eq. (2). By combining Eqs. (1) and (2), the mass ratio of T.Ca/T.O can be described as a function of $\text{Ca}_{\text{dissolved}}/\text{O}_{\text{oxide}}$, $\text{Ca}_{\text{oxide}}/\text{O}_{\text{oxide}}$, $\text{Ca}_{\text{CaS}}/\text{O}_{\text{oxide}}$ and $\text{O}_{\text{dissolved}}/\text{T.O}$, as expressed by Eq. (3), where $\text{Ca}_{\text{dissolved}}/\text{O}_{\text{oxide}}$ means the extent of modification of oxide inclusion

Fig. 1. Element mappings of typical inclusions detected in slab samples (a) a typical Al_2O_3 based inclusion; (b) a typical $\text{Al}_2\text{O}_3\text{-CaS}$ inclusion with a crescent shaped CaS layer; (c) a typical $\text{Al}_2\text{O}_3\text{-CaS}$ inclusion with a oval shaped CaS layer; (d) a typical better modified calcium aluminate; (e) a typical CaO-CaS inclusion.

Table 3. The composition of inclusions from 38 heats in slab samples.

No.	Inclusion type	MgO mass%	CaO mass%	Al ₂ O ₃ mass%	CaS mass%	Number density/mm ²	No.	Inclusion type	MgO mass%	CaO mass%	Al ₂ O ₃ mass%	CaS mass%	Number density/mm ²
1	CC	2.9	43.8	7.6	45.7	12.7	19	AC	10.7	3.6	45.5	40.2	13.5
2	CC	3.8	38.5	2.9	54.8	15.6	20	AC	10.7	1.8	44.6	42.9	10.2
3	CC	3.8	20.2	3.8	72.1	10.9	21	A	20.0	2.4	75.2	2.4	10.0
4	CC	2.0	44.1	5.9	48.0	13.6	22	CA	13.0	41.7	33.9	11.3	15.7
5	CC	2.0	45.1	1.0	52.0	12.5	23	AC	11.5	17.7	24.8	46.0	12.8
6	CC	3.8	21.2	2.9	72.1	12.4	24	AC	8.3	14.7	42.2	34.9	20.3
7	CC	5.7	19.8	5.7	68.9	13.1	25	CC	2.9	44.7	1.9	50.5	10.8
8	CC	3.8	12.5	10.6	73.1	11.8	26	AC	13.8	12.9	53.4	19.8	6.3
9	CC	2.9	22.3	3.9	70.9	14.9	27	A	18.0	4.1	70.5	7.4	8.7
10	CC	4.8	40.0	2.9	52.4	21.3	28	AC	21.9	10.2	50.8	17.2	14.5
11	AC	10.7	17.9	46.4	25.0	13.9	29	AC	9.1	13.6	59.1	18.2	29.4
12	AC	9.9	19.8	45.9	24.3	11.3	30	AC	13.8	12.1	56.9	17.2	30.1
13	AC	11.5	1.8	46.0	40.7	15.0	31	AC	10.7	12.5	42.0	34.8	36.4
14	AC	7.4	1.9	38.9	51.9	11.3	32	AC	5.7	17.9	49.1	27.4	9.9
15	AC	8.3	8.3	46.8	36.7	9.1	33	A	16.0	1.7	80.7	1.7	12.3
16	AC	11.5	2.7	46.9	38.9	4.4	34	AC	5.7	3.8	21.7	68.9	16.9
17	A	6.5	4.7	72.9	15.9	13.8	35	AC	4.8	6.7	23.8	64.8	19.2
18	A	9.1	10.9	68.2	11.8	20.5	36	AC	5.7	11.3	39.6	43.4	29.3

The number density equals the number of all the inclusions divided by scanning area.

Fig. 2. The distribution of inclusions composition in Al₂O₃-CaO-CaS or Al₂O₃-CaO-MgO ternary phase diagram (a) CaO-CaS inclusions from No. 1 slab sample; (b) Al₂O₃-CaS inclusions from No. 13 slab sample; (c) Al₂O₃ based inclusions from No. 27 slab sample.

by dissolved Ca in steel. Ca_{oxide}/O_{oxide} means the mass ratio of calcium to oxygen in oxides and its value is shown in **Table 4**, which assumes that oxide inclusion in steel is one of three typed inclusions including CA6, CA or C12A7, where C and A mean CaO and Al₂O₃ respectively. Ca_{CaS}/O_{oxide} means the mass ratio of calcium of CaS to oxygen of oxide inclusion and is regarded as zero because CaS is very difficult to generate in molten steel in the case of low sulfur content according to the results reported by Refs. 9), 10). The dissolved oxygen ($O_{dissolved}$) in molten steel before calcium treatment is determined by the equilibrium between Al in the steel and Al₂O₃ in the inclusions, as expressed by Eqs. (4) and (5) and $O_{dissolved}$ is given by Eq. (6), where the activity of Al₂O₃ has been reported by Ref. 8) and shown in Table 4.

$$T.Ca = Ca_{dissolved} + Ca_{oxide} + Ca_{CaS} \quad \text{..... (1)}$$

Table 4. The mass ratio of Ca_{oxide}/O_{oxide} and activity of Al₂O₃ in various calcium aluminates.

Oxide inclusion	CA6	CA	C12A7
Mass ratio of Ca_{oxide}/O_{oxide}	0.1316	0.6250	0.9091
Activity of Al ₂ O ₃ in CxAy inclusion	0.5102	0.2467	0.0536

$$T.O = O_{dissolved} + O_{oxide} \quad \text{..... (2)}$$

$$\frac{T.Ca}{T.O} = \frac{Ca_{dissolved} + Ca_{oxide} + Ca_{CaS}}{O_{dissolved} + O_{oxide}} = \left(\frac{Ca_{dissolved}}{O_{oxide}} + \frac{Ca_{oxide}}{O_{oxide}} + \frac{Ca_{CaS}}{O_{oxide}} \right) \cdot \left(1 - \frac{O_{dissolved}}{T.O} \right) \quad \text{... (3)}$$

$$\Delta G_1^\theta = -1225417 + 393.8T \dots\dots\dots (5)$$

$$O_{dissolved} = \left(\exp \left(\frac{\Delta G_1^\theta}{RT} \right) \frac{a_{Al_2O_3}}{f_{Al}^2 f_O^3 [mass\%Al]^2} \right)^{1/3} \dots\dots\dots (6)$$

Based on the experimental results shown in Tables 1–4 and Eqs. (1)–(6), the relation between T.Ca/T.O and $Ca_{dissolved}/O_{oxide}$ with various calcium aluminates is shown in Fig. 3. As shown, $Ca_{dissolved}/O_{oxide}$ increases with the increase of T.Ca/T.O and their relationship is close to a nearly liner indicating that T.Ca/T.O can show the extent of modification of alumina inclusions by calcium. Besides, it is noticed that $Ca_{dissolved}/O_{oxide}$ of CA6 is higher than $Ca_{dissolved}/O_{oxide}$ of C12A7 in the case T.Ca/T.O is constant. The main reason is that dissolved Ca in molten steel is equal to T.Ca minus undissolved Ca in inclusions according to Eq. (3) while undissolved Ca of CA6 is less than that one of C12A7. Actually, dissolved Ca of Eq. (3) should be equal or greater than the equilibrium Ca between steel and inclusions. So $Ca_{dissolved}/O_{oxide}$ of inclusions indicates the ease or complexity of inclusions being modified by dissolved Ca in molten steel. That is to say, low modified calcium aluminates with higher $Ca_{dissolved}/O_{oxide}$ are easier to be modified into better calcium aluminates by dissolved Ca in molten steel.

4.2. Effect of T.Ca/T.O on the MgO Content of Inclusions

For Al-killed steel, there are two manners for Al_2O_3 inclusions modification during LF refining: the first route is followed by $Al_2O_3 \rightarrow$ low modified calcium aluminates $\rightarrow$ liquid calcium aluminates and the other is as $Al_2O_3 \rightarrow MgO-Al_2O_3$ spinel $\rightarrow CaO-MgO-Al_2O_3$ multi-component inclusion. $MgO-Al_2O_3$ spinel is generated before calcium treatment and transfers into $CaO-Al_2O_3-MgO$ after calcium wire being fed, which has been demonstrated by researchers^{10–12)} and the process can be described by Eq. (7).

Fig. 3. The relationship between T.Ca/T.O and $Ca_{dissolved}/O_{oxide}$ with various calcium aluminates.

The relationship between T.Ca/T.O and MgO content in inclusions of all slab samples is shown in Fig. 4. It can be seen that MgO content in inclusions obviously decreases with the increase of T.Ca/T.O. In the case T.Ca/T.O is close to zero, MgO content in inclusions is 15–20%. In the case T.Ca/T.O is over 1.5, MgO content in inclusion is less 5%, which indicates that MgO content in inclusions was reduced by Ca being fed into molten steel.

4.3. Effect of T.Ca/T.O on Al_2O_3 Content of Inclusions

In order to better control inclusions composition, the relationship between Al_2O_3 content in inclusions and T.Ca/T.O is given and shown in Fig. 5, where the spots with the shape of box and solid triangle are reported by M. Numata *et al.*^{3,4)} and G. W. Yang *et al.*^{1,2)} respectively and their results is almost in accordance with the ones in present work in the case of T.Ca/T.O less than 1.5 and there exists a certain difference in the case of T.Ca/T.O over 1.5. Besides, it is divided into three parts including A, AC and CC respectively, by dot line based on T.Ca/T.O in steel. It can be seen that Al_2O_3 content of inclusions almost linearly decreases with the increase of T.Ca/T.O in steel. In the case of T.Ca/T.O in steel over 1.5, Al_2O_3 content in inclusions is very less, which means the type of inclusion is close to CaO–CaS complex inclusion; In the case of T.Ca/T.O in

Fig. 4. The relationship between T.Ca/T.O and MgO content in inclusions of all slab samples.

Fig. 5. The relationship between T.Ca/T.O and Al_2O_3 content in inclusion of all slab samples.

steel less than 0.5, Al_2O_3 content in inclusion is very high even close 90%, which indicates the type of inclusion is Al_2O_3 inclusion or low modified calcium aluminates; In the case of T.Ca/T.O in steel greater than 0.5 and less than 1.5, the type of inclusion is Al_2O_3 –CaS inclusion.

4.4. Effect of T.Ca/S on the Modification Extent of Al_2O_3 Inclusions

To clarify the effect of S content in molten steel on modification extent of Al_2O_3 inclusions by Ca, the relation between T.Ca/S and modification extent of inclusions was studied and shown in Fig. 6, where the modification extent of inclusions was expressed by the mole ratio of Ca content from CaO and CaS in inclusions to Al content of Al_2O_3 in inclusions. It can be seen that the mole ratio of Ca to Al ((mole%Ca)/(mole%Al)) in inclusion increases with the increase of T.Ca/S in steel, which means that increasing T.Ca/S in steel can significantly improve the modification extent of Al_2O_3 inclusions. If Al_2O_3 inclusions can be modified well into calcium aluminates, T.Ca/S in molten steel should be over 2.0, which means it is very difficult to modify alumina into well calcium aluminates in the case of more S content, which is accordance with the results of Ref. 5).

To understand the formation reason of CaS in complex inclusions, the relation between (mole%Ca)/(mole%Al) and CaS content of inclusions was studied and shown in Fig. 7. It is noticed that calcium of CaS in inclusions is contained in (mole%Ca) and the reason can be explained as following: Firstly, CaS in Al_2O_3 –CaS typed inclusions is mainly generated during casting solidification process and difficult to be formed in motel steel according to previous results of Ref. (8). Secondly, Calcium of CaS in inclusions has modified alumina into calcium aluminates in motel steel. So the ratio of (mole%Ca) of CaO and CaS in inclusions to (mole%Al) in inclusions can better represent for the modification extent of calcium aluminates. It can be seen that CaS content in inclusions increases with (mole%Ca)/(mole%Al) of inclusions, which indicates that higher (mole%Ca)/(mole%Al) of inclusion makes CaS content more. From the above, it is can be inferred that, under the condition of the same Ca content for different slab samples, higher sulfur content in

Fig. 6. The relationship between T.Ca/S and (mole%Ca)/(mole%Al) in inclusion.

steel suppresses the modification of Al_2O_3 inclusions by Ca and further makes less S content dissolve in complex inclusions and finally generates less CaS content in inclusions.

4.5. Effect of T.Ca on the Cleanness of Steel

In general, T.O content was considered as an important index to evaluate the cleanness of steel. The relationship between T.Ca and T.O is given in Fig. 8. It can be seen that T.O content doesn't change with T.Ca content in steel in the case of T.Ca less than 0.0018% and increases with T.Ca content in steel in the case of T.Ca over 0.0018%. It can be inferred that excess calcium treatment results in reoxidation of steel and the reason can be explained as follow.

Firstly, the liquid steel was easier to exposed to atmosphere during calcium wires being fed into molten steel because of its good activity under high temperature and then reoxidation occurred. Secondly, lots of impurities were introduced by Ca wires, whose composition in the industrial trials is shown in Table 5, which could make steel cleanness worse. Finally, before calcium treatment, the equilibrium

Fig. 7. The relationship between CaS content and (mole%Ca)/(mole%Al) in inclusion.

Fig. 8. The relationship between T.Ca and T.O content in inclusion.

Table 5. The composition of Ca wires in industrial trials.

Wire type	Ca content mass%	Si content mass%	Other mass%
Si–Ca wire	28	52	20
Ca wire	96	0	4

both dissolved aluminum and dissolved oxygen in molten steel can be described as Eq. (4). When amount of Ca wires was fed into molten steel, the Al–O equilibrium was broken and made chemical reaction continue toward the right side and generated more various calcium aluminates.

4.6. Formation Mechanism of Various Typed Inclusions

According to the above analysis, formation mechanisms of various typed inclusions are proposed.

4.6.1. Al_2O_3 Based Inclusions

For Al_2O_3 based inclusions, their formation mechanism could be described as following. At the end of LF refining, a small amount of Mg and Ca was generated in molten steel due to the feeding of Al alloy and reactions (8) and (9) took place, thus they reacted with existed Al_2O_3 inclusions to form MgO– Al_2O_3 spinel and low modified calcium aluminates respectively expressed by reactions (10) and (11), which has been reported by researchers.^{9–12)}

Meanwhile, only few or no Ca wires were fed into molten steel for heats with Al_2O_3 based inclusions, which made T.Ca content in molten steel was so less that reaction (11) was not sufficient. Moreover, the sulfur capacity of Al_2O_3 based inclusions is very less according to Ref. 8) based on KTH model, resulting that CaS was not easy to precipitate during solidification process.

4.6.2. Al_2O_3 –CaS Inclusions

For samples with Al_2O_3 –CaS inclusions in slab, a large amount of Ca wires were fed into molten steel, which makes T.Ca content was higher and then reactions (12) or (13) were taken place to generate better modified calcium aluminates based on the following reason: MgO content was decreased with the increase of T.Ca/T.O shown in Fig. 4, which indicates MgO in inclusions could be reduced by dissolved Ca to form CaO. Meanwhile, excess calcium made reaction (14) occur towards the right side of forming better modified calcium aluminates. Because well modified calcium aluminates have more sulfur capacity, which makes CaS component precipitate during solidification process based on the theory of previous research results.^{8,10)}

4.6.3. CaO–CaS Inclusions

For samples with CaO–CaS inclusions in slab, larger amount of Ca wires were fed into molten steel, which made reactions (12) and (13) continuously occurred resulting in no or few MgO content being detected. Moreover, reaction (14) would proceed towards the right side and formed better modified calcium aluminates. With the increase of modification extent of calcium aluminates, sulfur capacity of inclusions increased and Al_2O_3 –CaS inclusions would be formed if reaction (14) didn't proceed. However, for samples with CaO–CaS inclusions in slab, Ca content of molten steel was excess, which made reaction (14) occurred continuously and Al_2O_3 component of calcium aluminates was reduced gradually by Ca until few even no Al_2O_3 content. Finally, lots of CaO–CaS inclusions were generated.

5. Conclusion

Inclusions in slab samples with various T.Ca, T.O and S content were investigated in low carbon aluminum killed steel with low sulfur content based on industrial experiments and the relationship between steel and inclusions was studied by analyzing inclusions characteristic being detected by SEM-EDS. The following conclusions were obtained.

(1) T.Ca/T.O in steel could better replace dissolved Ca to evaluate the extent of modification of alumina inclusions by Ca.

(2) Inclusions changed from Al_2O_3 based inclusions to Al_2O_3 –CaS inclusions and finally to CaO–CaS inclusions with the increase of T.Ca/T.O in steel for slab samples and MgO and Al_2O_3 content in inclusions almost linearly decreased with T.Ca/T.O in steel.

(3) Increasing T.Ca/S in steel could improve the modification extent of alumina by Ca further increased CaS content of inclusions for slab samples with Al_2O_3 –CaS inclusions.

(4) The formation mechanism of inclusions including Al_2O_3 based inclusions, Al_2O_3 –CaS inclusions and CaO–CaS inclusions was discussed.

REFERENCES

- 1) G. W. Yang, X. H. Wang, D. Yang and X. Hao: *Metall. Mater. Trans. B*, **46B** (2015), 145.
- 2) G. W. Yang and X. H. Wang: *ISIJ Int.*, **55** (2015), 126.
- 3) M. Numata and Y. Higuchi: *ISIJ Int.*, **52** (2012), 2013.
- 4) M. Numata, Y. Higuchi and S. Fukagawa: *Tetsu-to-Hagane*, **84** (1998), 159.
- 5) S. K. Choudhary and A. Ghosh: *ISIJ Int.*, **48** (2008), 1552.
- 6) L. Holappa, M. Hämäläinen, M. Liukkonen, M. Lind and K. Tshilombo: *Ironmaking Steelmaking*, **30** (2003), 111.
- 7) H. Suito and R. Inoue: *ISIJ Int.*, **36** (1996), 528.
- 8) D. W. Zhao, H. B. Li, C. L. Bao and J. Yang: *ISIJ Int.*, **55** (2015), 2125.
- 9) M. Jiang, X. H. Wang, B. Chen and W. J. Wang: *ISIJ Int.*, **50** (2010), 95.
- 10) J. Guo, S. S. Cheng and Z. J. Cheng: *ISIJ Int.*, **53** (2013), 2142.
- 11) W. Yang, L. F. Zhang, X. H. Wang, Y. Ren, X. F. Liu and Q. S. Shan: *ISIJ Int.*, **53** (2013), 1401.
- 12) S. F. Yang, Q. Q. Zhang, L. F. Zhang, J. S. Li and K. Peaslee: *Metall. Mater. Trans. B*, **43B** (2012), 731.