Tracking Large-size Inclusions in Al Deoxidated Tinplate Steel in Industrial Practice

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(Received on November 5, 2020; accepted on March 16, 2021; J-STAGE Advance published date: May 15, 2021)

The three-dimensional morphology, size, content and composition of large-size inclusions extracted by large sample electrolysis from RH refining to hot rolling were investigated during the tinplate steel industrial test without calcium treatment. The results showed that the large-size inclusions in the RH refining process are Al_2O_3 inclusions and incompletely modified $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$ inclusions, while those in tundish are Al_2O_3 , $\text{CaO}\text{--}\text{Al}_2\text{O}_3$, $\text{CaO}\text{--}\text{SiO}_2\text{--}\text{Al}_2\text{O}_3$ and $\text{CaO}\text{--}\text{SiO}_2\text{--}\text{Al}_2\text{O}_3\text{--}\text{MgO}$. The typical types of large-size inclusion in slab and hot rolling plates are Al_2O_3 , $\text{CaO}\text{--}\text{Al}_2\text{O}_3$, $\text{SiO}_2\text{--}\text{Al}_2\text{O}_3$, $\text{CaO}\text{--}\text{SiO}_2\text{--}\text{Al}_2\text{O}_3$, $\text{CaO}\text{--}\text{SiO}_2\text{--}\text{Al}_2\text{O}_3\text{--}\text{MgO}$ and $\text{CaO}\text{--}\text{SiO}_2\text{--}\text{Al}_2\text{O}_3\text{--}\text{TiO}_2$. Secondary oxidation was found to occur in molten steel during the pouring process and protective casting should be improved. Large-size inclusions in hot rolling plates are Al_2O_3 with a mass fraction of 19.8% and incompletely modified $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$ inclusions with a mass fraction of 45.9% those have not been completely modified, which have high hardness and are difficult to deform. Therefore, it is recommended that calcium treatment should be carried out at the end of RH refining to reduce the Al_2O_3 and $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$ contents. And the effect of calcium addition on the inclusion evolution has been studied by a thermodynamic analysis at 1 873 K. With the increase of calcium addition in molten steel, the evolution route of equilibrium precipitations is $\text{Al}_2\text{O}_3 \rightarrow \text{CaO}\cdot 6\text{Al}_2\text{O}_3 \rightarrow \text{CaO}\cdot 2\text{Al}_2\text{O}_3 \rightarrow \text{CaO}\cdot \text{Al}_2\text{O}_3 \rightarrow 3\text{CaO}\cdot \text{Al}_2\text{O}_3 \rightarrow 12\text{CaO}\cdot 7\text{Al}_2\text{O}_3 \rightarrow \text{CaO}$. The critical calcium content for CaS and CaO formation increases with increasing oxygen content. To avoid the precipitation reaction between [Ca] and [S], the mass fraction of calcium addition needs to be controlled below 0.0040%.

KEY WORDS: tinplate steel; large-size inclusions; large sample electrolysis; calcium treatment.

1. Introduction

Tinplate steel is a typical type of hot-rolled material, which has the characteristics of strong oxidation resistance, high strength and good formability. It is widely used in food packaging and pharmaceutical packaging. Therefore, a high surface quality of tinplate steel plate is required and inclusion control plays a significant role in tinplate steel production.^{1–3)} Tinplate steel can be produced by various refining processes, such as RH refining, LF refining, and LF+RH refining.^{4,5)} In order to reduce the product cost, an increasing number of steel plants adopt RH refining for tinplate steel production.

Tinplate hot rolling plates produced in a domestic steel plant have cracks and surface defects due to large-size inclusions during the hot rolling process, especially those inclusions with high melting points, poor deformability and

size larger than 50 μm , and consequently, the continuity of tinplate hot rolling plates is destroyed and surface quality deteriorates. Therefore, removal and modification of the non-metallic large-size inclusions have been an important task during the steelmaking process.

Many research results have shown that the cracks and defects in tinplate hot rolling plates are usually caused by non-metallic large-size inclusions. However, the formation of large-size inclusions during the steelmaking process is inevitable because of the interactions of molten steel with slag and refractory.^{6–8)} It is generally considered that the inclusions exceeding a certain size are the main cause of surface quality problems. Large-size inclusions are less in number and are randomly distributed in steel, which has a great influence on the quality of tinplate steel products.^{7,8)}

Aluminum is used as a deoxidizer for tinplate steel and the main deoxidation products are Al_2O_3 inclusions, which has an adverse effect on the castability of molten steel, such as nozzle clogging.⁹⁾ Al_2O_3 inclusions with high

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melting points can be either modified into low-melting ones by calcium treatment to diminish the adverse effect or removed by floating to the ladle surface, or become defects of steel product.^{9–11)} Calcium treatment is a common approach to modify Al_2O_3 inclusions, and many research results have been reported both on industrial practice and laboratory experiments. The evolution path of alumina inclusion by calcium treatment can be described as $\text{Al}_2\text{O}_3 \rightarrow \text{CaO} \cdot 6\text{Al}_2\text{O}_3 \rightarrow \text{CaO} \cdot 2\text{Al}_2\text{O}_3 \rightarrow \text{CaO} \cdot \text{Al}_2\text{O}_3 \rightarrow 12\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3$.^{12,13)} Nevertheless, as calcium element has a strong affinity with oxygen and sulfur, calcium aluminate inclusions would also be modified into CaO and CaS inclusions if an excessive amount of calcium is added into molten steel. Hence, the application of calcium treatment possibly has an adverse effect on the steel properties if the additional amount of calcium is not well controlled.^{14,15)}

The common methods to detect inclusions include acid dissolution method, large sample electrolysis method and scanning electron microscope of ASPEX. Since the alumina-based inclusions are mostly irregular blocks and clustered shaped, the two-dimensional morphologies observed in the cross-section hardly reveal their real morphology, and the randomness of the metallographic microscope and scanning electron microscope is an important factor to cause big detection difference. Up to now, the characterizations of the three-dimensional morphology of non-metallic large-size inclusions in tinplate steels have been seldom reported. Large sample electrolysis is a method mainly used for the analysis of large-size inclusions larger than 50 μm . Large sample electrolysis extraction with the advantages of obtaining non-destructive inclusion and analysis of three-dimensional morphology, size and chemical composition is more reliable.¹⁶⁾ Therefore, in this work the large-size inclusions in tinplate steel were separated and extracted through large sample electrolysis, aiming at a better understanding of the formation and evolution of large-size inclusions, which is conducive to control and removal of inclusions.

In this paper, the content, size, composition and three-dimensional morphology of large-size inclusions from RH refining to hot rolling were systematically studied by large sample electrolysis experiments in industrial practice and the evolution of large-size inclusions in tinplate steel was ana-

lyzed. Besides, some effective measures of reducing and controlling large-size inclusions were proposed, which would contribute to improving the quality of tinplate steel products.

2. Experimental

2.1. Experiment and Sampling

Tinplate steel produced by a steel plant in China was selected as the research object. The industrial tests of tinplate steel were conducted through the production route of 180t BOF steelmaking $\rightarrow$ RH refining $\rightarrow$ Continuous casting $\rightarrow$ Hot rolling plate. The total oxygen content was 428 ppm at the blowing end-point of BOF and no deoxidant agent was added into the ladle for pre-deoxidation during the tapping process. Subsequently, the ladle was transported to the RH refining station and molten steel was degassed for 3 min. At the middle stage of RH refining process, MnFe alloy was added to adjust the composition of molten steel. The RH refining time was 20 min and the molten steel was gently stirred for 5 min by argon gas. In particular, no calcium treatment was carried out at the end of RH refining. The cross-section of the bloom was 1 000 mm $\times$ 230 mm and the casting speed was 1.29 $\text{m} \cdot \text{min}^{-1}$. Finally, the specimens were taken respectively after Al addition (Sample 1), end of RH refining (Sample 2), tundish (Sample 3), slab (Sample 4) and hot rolling plate (Sample 5). The schematic illustration of sampling is shown in Fig. 1.

2.2. Extraction of Inclusions and Sample Analysis

Steel and slag samples were prepared for chemical analy-

Fig. 2. Schematic diagram of large sample electrolysis experiment apparatus. (Online version in color.)

Fig. 1. Schematic illustration during the samplings process. (Online version in color.)

sis. The contents of acid-soluble [Al], [Ca], and [Mg] in steel samples were analyzed by ICP-AES. T.O content (total oxygen content) and T.N (total nitrogen content) content in the steel samples were determined by fusion and infrared absorption method.

Figure 2 is a schematic diagram of large sample electrolysis experiment apparatus. The large sample electrolysis process mainly includes sample electrolysis, ultrasonic cleaning, elutriation, drying, reduction and magnetic separation. The steel sample was used as the anode (cuboid, 50 mm × 50 mm × 170 mm), and a cylinder iron mesh attached to the edge of the electrolyzer was used as the cathode. Fe element in the steel sample lost electrons and became ions to enter into the electrolyte, and on the other hand, the inclusions in the steel sample precipitated to the anode slime. Then, the anode slime was collected and filtered through a filter to obtain inclusions after the electrolysis was completed. Electrolytes with 5% ZnCl₂, 0.3% HCl, 6% FeCl₂, 4% FeSO₄ and 0.5% citric acid were electrolyzed for 15–20 days. The steel samples were connected in series. The pH value of the solution was less than 5, and the temperature was below 303 K. The electric current density was about 0.03 A·cm⁻². In this work, the electrolytic process was performed under constant electric current to avoid breaking the inclusions in the steel sample. The inclusions with a size larger than 50 μm were extracted and gathered from the steel sample by filtering the electrolyte solution. The size and composition of the extracted large-size inclusions were analyzed by stereomicroscope and SEM-EDS.

3. Results and Discussion

3.1. Compositions of Steel and Slag

The chemical compositions of tinplate steel samples are listed in **Table 1** and the chemical compositions of auxiliary materials used in the industrial experiment are shown in **Table 2**.

T.O content is an important index to evaluate the steel cleanliness and T.N content can represent the re-oxidation by air absorption during the steelmaking process. To investigate the removal efficiency of inclusions by RH refining,

the T.O contents of Sample 1–Sample 4 were analyzed, as shown in **Fig. 3**. It can be noted that T.O content in molten steel decreased significantly after Al addition. T.O content is 428 ppm at the blowing end-point of BOF, whereas T.O content is 49 ppm in Sample 1. The T.O content decreased slightly from Sample 1 to Sample 2 through RH vacuum treatment and T.O content decreased by 30% after argon-blow stirring for 5 min, indicating that bottom blowing argon had a positive effect on inclusion removal.

Under the condition of high-basicity refining slag, (CaO) in the RH refining slag and MgO in the magnesium-based refractory can be reduced by dissolved [Al] and [Ca] and [Mg] are generated in molten steel after Al addition, as expressed in Eqs. (1) and (2). Besides, [Al] content decreased by 0.016% from Sample 1 to Sample 4 and Al₂O₃ inclusions would generate in molten steel. It can be also found that T.N content decreased from 0.0018% to 0.0012%, indicating that there is no reoxidation of molten steel during the RH refining process.

Fig. 3. T.O and T.N content of molten steel in Sample 1–Sample 4. (Online version in color.)

Table 1. Chemical composition of steel samples during the RH refining process (mass%).

Sample	[C]	[Si]	[Mn]	[P]	[S]	[Al]	[Ca]	[Mg]	T.O	T.N
Sample 1	0.042	0.001	0.137	0.013	0.008	0.052	0.0006	0.0005	0.0049	0.0018
Sample 2	0.029	0.003	0.182	0.014	0.008	0.046	0.0019	0.0008	0.0037	0.0013
Sample 3	0.015	0.006	0.176	0.014	0.008	0.037	0.0024	0.0010	0.0063	0.0023
Sample 4	0.013	0.010	0.170	0.014	0.008	0.029	0.0020	0.0010	0.0029	0.0024

Table 2. Chemical composition of auxiliary materials (mass%).

Name	CaO	Al ₂ O ₃	MgO	SiO ₂	Fe ₂ O ₃	K ₂ O	Na ₂ O	TiO ₂	F-	C	Other
RH refining slag	54.46	31.66	5.01	8.87	—	—	—	—	—	—	0
Tundish covering flux	44.27	0.48	1.45	52.47	0.41	—	—	—	—	6.31	Balance
Mold fluxes	30.98	4.67	1.82	35.55	4.22	4.08	5.86	0.91	6.43	5.38	Balance
Filler sand	0	20.44	7.06	25.30	25.64	3.23	3.09	0.27	0.88	—	Balance

3.2. Content and Size Distribution of Large-Size Inclusions in Tinplate Steel

The large-size inclusion content is calculated based on the mass of the inclusions obtained by large sample electrolysis with a size larger than 50 μm per unit weight of steel, as expressed in Eq. (3).

$$I = \frac{M_2}{M_1} \times 10^4 \dots\dots\dots (3)$$

where M_1 is the mass of electrolytic steel sample, g; M_2 is the mass of inclusions obtained by large sample electrolysis, g; I is the large-size inclusions content in steel, $\text{mg} \cdot (10\text{kg})^{-1}$

Table 3. Mass large-size inclusions in Sample 1–Sample 5.

Sample	M_1	M_2	I	50–100 μm	100–180 μm	>180 μm
				mg	mg	mg
Sample 1	846	5.000	59.102	3.20	1.50	0.30
Sample 2	1 040	0.800	7.692	0.42	0.21	0.17
Sample 3	1 147	0.900	7.847	0.58	0.32	0
Sample 4	2 085	2.000	9.592	1.28	0.54	0.18
Sample 5	1 900	1.000	5.263	0.48	0.28	0.24

$\text{kg})^{-1}$.

The macro-morphology of large-size inclusions in tinplate steel is detected by stereo-microscope, as shown in Fig. 4. The statistical results of large-size inclusions by large sample electrolysis are shown in Table 3 and Fig. 5. Table 3 shows the mass and size of the large-size inclusions in Sample 1–Sample 5. According to the mass of inclusions in each steel sample, the content of large-size inclusion electrolyzed can be obtained through integration, as shown in Fig. 5(a). Figure 5(b) is the histogram of the mass fraction of large-size inclusions with different sizes. It can be noted that the average sizes of all inclusions are far larger than those tested by the automatic detection system according to reference 17).

It can be seen in Figs. 5(a) and 5(b) that the large-size inclusions content in Sample 1 reaches $59.102 \text{ mg} \cdot (10\text{kg})^{-1}$ after Al addition, and the mass fraction of inclusions with the size of 50–100 μm is 65%. The content of large-size inclusions in Sample 2 is $7.692 \text{ mg} \cdot (10\text{kg})^{-1}$, which is significantly reduced by 87%. From Sample 1 to Sample 2, the content of large-size inclusions with the size of 50–100 μm decreases, whereas the content of large-size inclusions with a size larger than 180 μm increases, which can be considered that some inclusions with the size of 50–100 μm collide

Fig. 4. Macro-morphology of large-size inclusions in Sample 1–Sample 5. (Online version in color.)

Fig. 5. Content and mass fraction of large-size inclusions in Sample 1–Sample 5. (Online version in color.)

and float to the ladle surface. There is no significant change in the large-size inclusions content between Sample 2 and Sample 3, but no large-size inclusions with a size larger than $180\text{ }\mu\text{m}$ are detected in Sample 3, indicating that the larger the size of inclusion in steel, the easier it will float to tundish covering flux and be adsorbed. The main reason is

Fig. 6. Relation curve between diameter and floating time of inclusions. (Online version in color.)

that large-size inclusions are easy to collide, aggregate and be removed. The content of large-size inclusions in Sample 4 increases slightly, which could be caused by the entrapment of mold fluxes. The content of large-size inclusions in Sample 5 is reduced by 45% compared with Sample 4, possibly caused by the deformation of cluster alumina and composite inclusions with a low melting point during the hot rolling process. Large-size inclusions are broken into many small size ones, which are filtered out during the elutriation process in large sample electrolysis.

The relationship between the inclusion diameter and floating time to the ladle surface can be calculated by Stokes law. The calculation conditions are taken as: molten steel temperature of 1873 K , molten steel density of $7200\text{ kg}\cdot\text{m}^{-3}$, inclusion density of $2900\text{ kg}\cdot\text{m}^{-3}$, molten steel viscosity of $1.9\times 10^{-3}\text{ kg}\cdot(\text{m}\cdot\text{s})^{-1}$, and ladle depth of 3.15 m . The calculated results are shown in Fig. 6. It can be noted that the inclusions with the diameters larger than $92\text{ }\mu\text{m}$, $65\text{ }\mu\text{m}$ and $50\text{ }\mu\text{m}$ can float to the ladle surface after 5 min, 10 min, and 17 min, respectively, indicating that not all the inclusions with a diameter larger than $50\text{ }\mu\text{m}$ can float to the surface completely after 5 min soft blowing under present process conditions. The existence of large-size inclusions in Sample 2 and Sample 3 confirms the theoretical calculation results. Therefore, the soft blowing time should be appropri-

Table 4. Composition and morphology of typical large-size inclusions in Sample 1–Sample 5.

Inclusions	Type	Composition of inclusions, mass%							Width (μm)	Morphology
		CaO	Al ₂ O ₃	MgO	SiO ₂	Na ₂ O	K ₂ O	TiO ₂		
Al ₂ O ₃	#a	0	99.71	0	0.15	0	0	0	137
CaO–Al ₂ O ₃	#b	22.42	77.38	0	0.20	0	0	0	125
CaO–SiO ₂ –Al ₂ O ₃	#c	40.18	38.62	1.35	18.85	0	0	0	80
CaO–MgO–SiO ₂ –Al ₂ O ₃	#d	34.05	8.25	44.72	10.97	0	0	0	85
SiO ₂ –Al ₂ O ₃	#e	0	32.43	0	56.61	10.96	1.96	0	110
CaO–SiO ₂ –Al ₂ O ₃ –TiO ₂	#f-1	14.42	9.56	0	42.17	6.21	2.19	5.76	100
CaO–SiO ₂ –Al ₂ O ₃ –TiO ₂	#f-2	23.34	39.43	3.97	9.12	0.97	3.02	15.57	220

ately extended, which would effectively reduce the surface defects of hot rolled plates.

3.3. Type and Source of Large-Size Inclusions in Tin-plate Steel

The EDS analysis results and classifications of typical large-size inclusions extracted in Sample 1–Sample 5 are shown in **Tables 4** and **5** respectively and the following information can be concluded in Table 4. The large-size inclusions are classified into six types according to chemical composition, numbered #a, #b, #c, #d, #e, #f.

(1) During the RH refining process, most of the large-size inclusions in Sample 1 and Sample 2 are irregular single-block (#a) and (#b) CaO–Al₂O₃ inclusions after Al addition, which are the generated deoxidation products. The largest Al₂O₃ inclusions shown in Table 5 are generally irregular blocks with a large number of pores on the surface. The

largest and average widths of Al₂O₃ inclusions in Sample 1 are 137 μm and 117 μm , while the largest and average widths of CaO–Al₂O₃ inclusions in Sample 1 are 125 μm and 119 μm respectively. According to the composition of CaO–Al₂O₃ inclusions in Table 4, it can be inferred that this type of CaO–Al₂O₃ inclusions is CaO 2Al₂O₃ referring to the CaO–Al₂O₃ phase diagram. The different shapes of the inclusions can be attributed to the different growth mechanisms of inclusion with different size ranges. When the size of inclusions is small, the growth is controlled by Brownian collision and diffusion, whereas the growth of large-size inclusions is controlled by turbulence collision.

(2) Some CaO–SiO₂–Al₂O₃ system inclusions (#c) with the largest and average widths of 80 μm and 72 μm respectively, are detected in Sample 3, which mainly come from the entrapment of the tundish covering flux.

(3) Some inclusions in Sample 3 are the irregular block CaO–MgO–SiO₂–Al₂O₃ system inclusions (#d) with the largest and average widths of 85 μm and 83 μm respectively, which mainly come from the reactions of the deciduous refractory. MgO-rich refractory is extensively used in the linings of ladle and tundish in the industrial production process.

(4) SiO₂–Al₂O₃ inclusions (#e) in Sample 4 and Sample 5 contain more than 50% SiO₂ and oxides of K and Na (total content is about 10%). According to the inclusion composition, it can be concluded that this type of inclusions could be filler sand usually composed of SiO₂, Al₂O₃, Na₂O and K₂O. This type of silicate inclusion generally has large particles, and their melting points are determined by the proportion of SiO₂ in the composition. The larger the proportion of SiO₂, the higher melting point of silicate inclusions. The largest and average widths of this type of inclusions are 110 μm and 55 μm , respectively.

(5) Some TiO₂ are detected in CaO–SiO₂–Al₂O₃ system inclusions (#f), and there are two main sources of TiO₂ in inclusions: one is the formation of secondary oxidation of molten steel, while the other is that the entrapment of mold fluxes, which contains a small amount of TiO₂. Based on the EDS analysis results, the mass fraction of TiO₂ in the inclusion is about 5–15%. It is mainly derived from the reactions of the involved mold fluxes. This type of inclusions is not easy to deform and usually causes surface quality problems during the hot rolling process. The largest and average widths of this type of inclusions in Sample 5 are 220 μm and 107 μm , respectively.

The formation and average widths of large-size inclusions in Sample 1–Sample 5 are given in Table 5, and the following information can be obtained from Table 5. The average and largest widths of large-size inclusions in Sample 1 are significantly larger than those in Sample 2–Sample 4, whereas those in Sample 5 are the smallest. The sizes of large-size inclusions obtained from large sample electrolysis are significantly larger than those detected by metallographic microscope. The main formation is as the followings: (i) Al₂O₃ inclusions from deoxidizing products; (ii) inclusions from the reactions of RH refining slag; (iii) inclusions from the entrapment of the tundish covering flux; (iv) inclusions from the reactions of deciduous refractory; (v) inclusions from the filler sand; (vi) inclusions from reactions of the entrapped mold fluxes.

Table 5. Formation and size of typical large-size inclusions in Sample 1–Sample 5.

Steel Sample	Type	Formation	Average width (μm)	Amount percentage
Sample 1	#a	Deoxidation products	117	84.6%
	#b	Reactions of RH refining slag	119	15.4%
Sample 2	#a	Deoxidation products	110	63.2%
	#b	Reactions of RH refining slag	112	36.8%
Sample 3	#a	Deoxidation products	105	29.7%
	#b	Reactions of RH refining slag	108	39.0%
	#c	Entrapment of tundish covering flux	72	17.1%
	#d	Reactions of the deciduous refractory	83	14.2%
	#e	Inclusions from the filler sand	79	4.0%
Sample 4	#a	Deoxidation products	94	35.6%
	#b	Reactions of RH refining slag	101	42.1%
	#c	Entrapment of the tundish covering flux	64	8.5%
	#d	Reactions of the deciduous refractory	76	7.3%
	#e	Inclusions from the filler sand	79	4.0%
Sample 5	#f-1, #f-2	Reactions of the entrapped mold fluxes	134	2.5%
	#a	Deoxidation products	87	19.8%
	#b	Reactions of RH refining slag	98	45.9%
	#c	Entrapment of the tundish covering flux	58	9.8%
	#d	Reactions of the deciduous refractory	72	10.9%
	#e	Inclusions from the filler sand	63	8.4%
	#f-1, #f-2	Reactions of the entrapped mold fluxes	107	5.2%

Fig. 7. Composition distribution of large-size inclusions in Sample 1–Sample 5. (Online version in color.)

3.4. Change of Size and Type of Large-Size Inclusions during Tinplate Steel Production

Moreover, the compositions of different types of inclusions in the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ ternary phase diagram calculated by FactSage software are shown in Fig. 7. The black line is calculated by FactSage 7.0 in which is the liquid region below 1 673 K. The inclusions in this region are fully liquid, while those outside this region are solid ones.

It can be found that the inclusions obtained in Sample 1 and Sample 2 are mainly Al_2O_3 inclusions and incompletely modified $\text{CaO-Al}_2\text{O}_3$ inclusions. The CaO and SiO_2 contents in Sample 3 increase gradually, which is mainly due to the reactions of the entrapped tundish covering flux or deciduous refractory. And the distribution of inclusions in the ternary $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ system phase diagram gradually approaches to the low melting point region. The number of inclusions in the region with a low melting point increases, indicating that the lower the melting point of inclusions, the higher the removal rate of inclusions. However, the Al_2O_3 inclusions content in Sample 4 significantly increases, indicating that secondary oxidation occurred in molten steel during the pouring process and the protective casting should be improved. On the contrary, the number of inclusions in the low melting point region of Sample 5 decreases mainly because the inclusions with a low melting point are easy to deform and break into small ones during the hot rolling process. The proportion of inclusions with a size of 50–100 μm decreases and the proportion of inclusions with size larger than 100 μm increases.

There are more limitations in the evaluation of inclusions by metallographic microscope. The size of inclusions obtained by large sample electrolysis is far larger than that detected by metallographic microscope. There exist great differences in the formation of inclusions based on different detection methods. Most internal inclusions are found by metallographic microscope whereas most external inclusions are found by large sample electrolysis, which are from

the entrapment of tundish covering flux, mold fluxes and deciduous refractory with deoxidizing products in molten steel. The accurate morphology and size of inclusions are obtained by large sample electrolysis extraction method, and Al_2O_3 and $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$ content in hot rolling plates could be used to evaluate directly the quality of production.

From the above results based on the present industrial test without calcium treatment, it can be found that the content of incompletely modified $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$ inclusions with high melting point obtained by large electrolysis samples in Sample 5 is the largest, and meanwhile, Al_2O_3 inclusions with a mass fraction of 19.8% were also detected, indicating that most of the Al_2O_3 inclusions have not been modified into the low melting point inclusions or removed by floating to the ladle surface during RH refining process. Al_2O_3 inclusions and $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$ inclusions can cause nozzle blockage during continuous casting and inclusion-related surface defects. Therefore, calcium treatment should be carried out at the end of RH refining to reduce the contents of Al_2O_3 and $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$ inclusions in molten steel. Therefore, in the following section, a thermodynamic analysis on the equilibrium precipitated phase in molten steel with calcium treatment would be carried out to clarify the importance of calcium treatment for Al-killed steels.

3.5. Thermodynamic Analysis on Equilibrium Precipitated Phase with Calcium Treatment

The chemical compositions of molten steel are listed in Table 1 and the chemical compositions of the RH refining slag used in the industrial test are shown in Table 2. The dissolved oxygen content in molten steel is calculated to be about 0.87 ppm according to Eqs. (4)–(5).^{18,19)} In the calculations, it is assumed that the generated Al_2O_3 inclusions are in equilibrium with Al_2O_3 in the RH refining slag, the activity of Al_2O_3 was considered as 0.02 at 1 873 K calculated by FactSage 7.0.

Fig. 8. Effect of calcium content on the equilibrium precipitation of inclusions at 1 873 K. (Online version in color.)

Table 6. Reactions at different zones.

Zones	Reaction	Equation
I	$[Ca] + 19/3 Al_2O_3 = CaO \cdot 6Al_2O_3 + 2/3 [Al]$	(6)
II	$[Ca] + 1/3 Al_2O_3 + 1/2 (CaO \cdot 6Al_2O_3) = 3/2 (CaO \cdot 2Al_2O_3) + 2/3 [Al]$	(7)
III	$[Ca] + 1/3 Al_2O_3 + (CaO \cdot 2Al_2O_3) = 2(CaO \cdot Al_2O_3) + 2/3 [Al]$	(8)
IV	$[Ca] + 2(CaO \cdot Al_2O_3) = (3CaO \cdot Al_2O_3) + 2/3 Al_2O_3 + 2/3 [Al]$	(9)
V	$[Ca] + 5/3 Al_2O_3 + (3CaO \cdot Al_2O_3) = 1/3 (12CaO \cdot 7Al_2O_3) + 2/3 [Al]$	(10)
	$[Ca] + [S] = CaS$	(11)
VII and VIII	$[Ca] + 1/21 (12CaO \cdot 7Al_2O_3) = 11/7 CaO + 2/3 [Al]$	(12)

$$2[Al] + 3[O] = (Al_2O_3) \quad \log K = -20.57 + 64\,000/T \dots (4)$$

$$K = \frac{a_{Al_2O_3}}{a_{[Al]}^2 \cdot a_{[O]}^3} \dots (5)$$

Al_2O_3 , $CaO \cdot Al_2O_3$, $CaO \cdot 2Al_2O_3$ and $CaO \cdot 6Al_2O_3$ inclusions with high melting points have high hardness and are difficult to be deformed during the hot rolling process, which are the key factors to cause surface quality problems. To explore the equilibrium precipitated phase after calcium addition a thermodynamic calculation is carried out at 1 873 K by FactSage 7.0 with databases of FactPS, FToxide and FTmisc.^{20,21)} Figure 8 shows the effect of calcium addition on the equilibrium precipitations in Fe-0.18%Mn-0.0037%O-0.003%Si-0.046%Al-0.008%S molten steel system, including the original oxygen content, 0.005%O, 0.010%O. When the oxygen content is 0.0037%, 0.005% and 0.010%, in order to control the inclusion composition of $12CaO \cdot 7Al_2O_3$, the critical calcium content has to be controlled below 40 ppm, 54 ppm and 108 ppm, respectively, as shown in Figs. 8(a), 8(b), 8(c). Under the present conditions of liquid steel composition, it can be seen that the range of Ca contents should be controlled between 26 and 40 ppm. It is so narrow and appears very difficult to control into the recommended ranges in practice. To expand the range of the calcium treatment, therefore, the molten steel should be desulfurized as much as possible under the present conditions of liquid steel composition. According to

Fig. 9. Effect of total oxygen on the critical Ca content to form CaS and CaO. (Online version in color.)

the characteristics of precipitations in steel, the evolution of inclusions can be divided into 8 zones and related reactions are presented in Table 6.

At zone I, Al_2O_3 and $CaO \cdot 6Al_2O_3$ are the equilibrium precipitations. The mass fraction of $CaO \cdot 6Al_2O_3$ increases with the decrement of Al_2O_3 , indicating that the equilibrium precipitation transfers from Al_2O_3 to $CaO \cdot 6Al_2O_3$, expressed by Eq. (6).²²⁾

At zone II, $CaO \cdot 6Al_2O_3$ and $CaO \cdot 2Al_2O_3$ are the equilibrium precipitations, and then $CaO \cdot 6Al_2O_3$ inclusions are modified to $CaO \cdot 2Al_2O_3$ with the increase of calcium content, expressed by Eq. (7), leading to a decrease in the mass fraction of $CaO \cdot 6Al_2O_3$.^{23,24)}

At zone III, $CaO \cdot 2Al_2O_3$ and $CaO \cdot Al_2O_3$ inclusions exist in the molten steel. With the increase of calcium addition, the mass fraction of $CaO \cdot Al_2O_3$ increases while the mass fraction of $CaO \cdot 2Al_2O_3$ decreases, expressed by Eq. (8).²⁵⁾

At zone IV, $CaO \cdot Al_2O_3$ and $3CaO \cdot Al_2O_3$ inclusions exist in the molten steel. With the increase of calcium content, the mass fraction of $3CaO \cdot Al_2O_3$ increases while the mass fraction of $CaO \cdot Al_2O_3$ decreases, expressed by Eq. (9).²⁴⁾

At zone V, $3CaO \cdot Al_2O_3$ and $12CaO \cdot 7Al_2O_3$ are the equilibrium precipitations. $3CaO \cdot Al_2O_3$ inclusions are modified to $12CaO \cdot 7Al_2O_3$, expressed by Eq. (10).

At zone VI, $12CaO \cdot 7Al_2O_3$ is the equilibrium precipitation, which has the lowest melting point among all calcium aluminate.

At zone VII and VIII, the calcium content is higher, and

CaO and CaS are the equilibrium precipitations. With the increase of calcium content in molten steel, CaO inclusion begins to exist in steel and the mass fraction of CaS increases through Eqs. (11) and (12).^{25,26)} To avoid the precipitation of CaS through the direct reaction between [Ca] and [S], the addition of calcium needs to be strictly controlled. According to the thermodynamic calculation, the mass fraction of calcium should be controlled below 0.0040%.

Based on the analysis mentioned above, as the increase of calcium addition into molten steel, the evolution route of equilibrium precipitations can be expressed as $\text{Al}_2\text{O}_3 \rightarrow \text{CaO} \cdot 6\text{Al}_2\text{O}_3 \rightarrow \text{CaO} \cdot 2\text{Al}_2\text{O}_3 \rightarrow \text{CaO} \cdot \text{Al}_2\text{O}_3 \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \rightarrow 12\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \rightarrow \text{CaO}$, which is in good agreement with the results reported in Al deoxidized steel.^{19,27–32)}

Furthermore, the effect of T.O on the critical Ca content to form CaS and CaO is studied, as shown in Fig. 9. From Fig. 9, the critical calcium contents for the formation of CaS and CaO are 40 ppm and 86 ppm under the present conditions of liquid steel composition, respectively. The critical calcium content changes with the total oxygen content in the molten steel. The critical calcium content for CaS and CaO formation increases with increasing oxygen content. The main reason is that the total oxygen content first affects the critical calcium content for the formation of liquid calcium-aluminates, which then leads to the change of the critical calcium content for the formation of CaS and CaO.

4. Conclusions

The content, size, composition and three-dimensional morphology of large-size inclusion in tinplate steel have been systematically studied by large sample electrolysis, and the conclusions are summarized as follows.

(1) In the present industrial experiment without calcium treatment, large-size inclusions in the RH refining process are Al_2O_3 inclusions and incompletely modified $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ inclusions, while those in tundish are Al_2O_3 , $\text{CaO} \cdot \text{Al}_2\text{O}_3$, $\text{CaO} \cdot \text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ and $\text{CaO} \cdot \text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{MgO}$ inclusions. The types of large-size inclusion in slabs and hot rolling plates are Al_2O_3 , $\text{CaO} \cdot \text{Al}_2\text{O}_3$, $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$, $\text{CaO} \cdot \text{SiO}_2 \cdot \text{Al}_2\text{O}_3$, $\text{CaO} \cdot \text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{MgO}$ and $\text{CaO} \cdot \text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{TiO}_2$. The large-size inclusions content is increased by 70% from the end of RH refining to tundish, indicating that secondary oxidation in molten steel during the pouring process and protective casting should be improved.

(2) For the present industrial experiment without calcium treatment, the large-size inclusions in hot rolling plates are Al_2O_3 with a mass fraction of 19.8% and incompletely modified $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ inclusions with a mass fraction of 45.9% those have not been completely modified, which are the key factors to cause surface quality problems during hot rolling process in the present industrial experiment without calcium treatment. Thus it is needed to carry out calcium treatment at the end of RH refining to reduce the contents of Al_2O_3 and $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$.

(3) Calcium treatment is recommended for the present RH refining process, and the effect of calcium addition on the inclusion evolution has been studied by a thermodynamic analysis at 1 873 K. With the increase of calcium

addition into molten steel, the evolution route of equilibrium precipitations is $\text{Al}_2\text{O}_3 \rightarrow \text{CaO} \cdot 6\text{Al}_2\text{O}_3 \rightarrow \text{CaO} \cdot 2\text{Al}_2\text{O}_3 \rightarrow \text{CaO} \cdot \text{Al}_2\text{O}_3 \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \rightarrow 12\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \rightarrow \text{CaO}$. The critical calcium content for CaS and CaO formation increases with the increment of oxygen content. To avoid the precipitation reaction between [Ca] and [S], the mass fraction of calcium addition should be controlled below 0.0040%.

Acknowledgments

This work was supported by the National Key R&D Program of China [Grant numbers 2016YFB0300602, 2017YFB0304203 and 2017YFB0304201] and National Natural Science Foundation of China [Grant numbers 51774072, 51774073 and 51974080].

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