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Dependence of the Clogging Possibility of the Submerged Entry Nozzle during Steel Continuous Casting Process on the Liquid Fraction of Non-Metallic Inclusions in the Molten Al-Killed Ca-Treated Steel

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Abstract: In the current study, the nozzle clogging behavior and inclusion composition in Al-killed Ca-treated steels were observed to investigate the relationship between the liquid fraction of non-metallic inclusions and the clogging possibility of the submerged entry nozzle. Clogging materials were mainly MgO-Al₂O₃ with less than 20% liquid phases, while most of the inclusions were full liquid CaO-Al₂O₃-MgO in tundish at the casting temperature. Thus, it was proposed that the nozzle clogging can be effectively avoided by modification of solid inclusions to partial liquid ones rather than full liquid ones. There was a critical value of liquid fraction of inclusions causing the nozzle clogging. A critical condition of the inclusion attachment on the nozzle wall was a function of $\cos \theta_{N-S} + \cos \theta_{I-S} < 0$. With the increase of T.Ca content in steel, the evolution route of inclusions was solid MgO-Al₂O₃-MigO and CaO-Al₂O₃-MigO and CaO. To avoid the clogging of the submerged entry nozzle (SEN) under the current casting condition, the appropriate T.Ca concentration range in Al-killed Ca-treated steels can be enlarged from the 100% liquid inclusion zone of 10–14 ppm to the 20% liquid inclusion zone of 4–38 ppm.

Keywords: submerged entry nozzle clogging; inclusions; liquid fraction; contact angle; Al-killed Ca-treated steels

1. Introduction

The submerged entry nozzle (SEN) is the key lining refractory to connect the tundish and the mold during steel continuous casting (CC) [1–3]. The attachment of non-metallic inclusions on SEN may lead to clogging, which is detrimental to the cleanliness and the castability of the steel during CC [4,5]. The SEN clogging leads to an unsteady fluid flow of the molten steel in the mold, causing the entrainment of mold flux [6]. Large clogging material particles result in the defect of the steel product, if being dislodged from the SEN and entering the mold with the molten steel [7]. Serious clogging may fully block the outports of the SEN and interrupt the casting process [5]. Therefore, it is of importance to investigate the cause of the SEN clogging during the steel CC process.

Many studies have been performed and reported to investigate and propose the mechanism of SEN clogging, including the attachment of solid inclusions [8,9], the reaction between the molten steel



and the nozzle material [10–13], the generation of new inclusions due to the reoxidation of the molten steel [14], and the initial frozen steel layer along the inside wall of the SEN nozzle [15,16]. Commonly, the clogging material on the wall of SEN was mainly composed of solid inclusions with high melting temperatures, such as Al₂O₃, MgOAl₂O₃, etc. To prevent the SEN clogging during the CC process, many strategies have been suggested, such as calcium treatment, argon blowing, optimizing nozzle shape, and preheating SEN [17,18]. Calcium wire injection (Ca treatment) is an effective way to modify Al₂O₃ and MgOAl₂O₃ solid inclusions to calcium aluminates with a lower melting temperature and avoid the nozzle clogging [19–25]. Traditionally, inclusions in Al-killed Ca-treated steels were modified to full liquid by Ca treatment to avoid the SEN clogging [26–28], while the insufficient and excess Ca can only partially modify inclusions to liquid ones [29,30]. Recently, it was found that the full liquid calcium aluminate inclusions gave rise to the linear string defects after the rolling process. Thus, the partial liquid calcium aluminate was the target composition of inclusions in Al-killed Ca-treated steels [31]. However, it is still unclear if the partial liquid Al₂O₃-CaO inclusions clogged the SEN during the casting process.

In the current study, to reveal the relationship between inclusion liquid fraction and submerged entry nozzle clogging during the CC of Al-killed Ca-treated steels, the nozzle clogging behavior and inclusion composition were analyzed using automated SEM/EDS inclusion analysis (ASPEX). The formation of inclusions was calculated using FactSage thermodynamic software.

2. Production Process of the Steel and Analysis of Non-Metallic Inclusions in the Steel

A plant trial for the production of Al-killed Ca-treated steels was performed. The production route was "Basic Oxygen Furnace (BOF) \rightarrow Ladle Furnace (LF) \rightarrow Ruhrstahl–Hereaeus (RH) \rightarrow Ca treatment \rightarrow CC". During the tapping of BOF, deoxidation was widely used to lower the oxygen in the molten steel. Aluminum was added for the steel deoxidation, leading to the formation of inclusions in the steel. High basicity slag was used to improve the deoxidation and desulfuration of the molten steel. The RH vacuum treatment was carried out following the LF refining process. Calcium treatment was adopted to modify inclusions. The slab dimension was 1450 × 230 mm². The average pouring temperature was 1796 K. The argon blowing rate from the top the SEN was 6–8 NL/min. The CaO-Al₂O₃-based mold flux was used. The casting speed was 1.3 m/min. During the CC process, a steel sample was taken at the outlet position in tundish during the steady casting in each heat during a CC sequence of eight heats.

The molten steel sample was quenched in water to avoid the inclusion transformation during the solidification and cooling of the molten steel. The taken steel sample was for the inclusion analysis and the steel chemical composition analysis. For the sample taken in the tundish, at least 300 inclusions in each sample were detected using automated scanning electron microscopy with energy dispersive X-ray (SEM/EDS) (FEI, Hillsboro, OH, USA) inclusion analysis (ASPEX) to obtain the amount, composition, and size of inclusions. The minimum detectable size of inclusions was 1.5 μ m. The total aluminum (T.Al), magnesium (T.Mg), and calcium contents (T.Ca) of steel were analyzed using inductively coupled plasma emission spectrometry (ICP). The total oxygen (T.O) of the steel was analyzed using a Leco analyzer (Leco, St. Joseph, MO, USA). The other chemical compositions of the bulk steel were analyzed using a spark-OES. The average chemical composition of Al-killed Ca-treated steels was shown in Table 1. The T.Ca in the current Al-killed Ca-treated steel was in the range of the 9–12 ppm.

Table 1. Average chemical composition of the Al-killed Ca-treated steel in the current study (wt%).

| (C) | (Si) | (Mn) | T.S | T.O | T.Al | T.Mg | T.Ca |
|------|------|------|--------|--------|-------|--------|--------|
| 0.06 | 0.23 | 1.6 | 0.0014 | 0.0015 | 0.035 | 0.0004 | 0.0012 |

3. Analysis of SEN Clogging Materials

A SEN after a four heats casting sequence as shown in Figure 1a was analyzed to investigate the clogging mechanism of the SEN of Al-killed Ca-treated steels. In Figure 1b, the nozzle was cut from

the center of SEN. It was seen that there was a clogging material layer on the inside wall of the SEN, as shown in Figure 1c. There, clogging material was taken from positions 1–3 on the inside wall of the SEN to analyze their morphologies and compositions using SEM-EDX. A sample was taken in position 4 to identify the composition distribution form the clogging surface to the nozzle matrix using elemental mapping using SEM-EDX.



Figure 1. Image of the SEN clogging and schematic sampling locations. (**a**) outside morphology, (**b**) inside morphology, (**c**) schematic.

Figure 2 shows the morphology of clogging materials at positions 1–3 of the SEN. In Figure 2a,b, the SEM images of attachment samples taken from positions 1 and 2 on the inside wall of the SEN presented coral-shaped clusters after the casting of the Al-killed Ca-treated steel. The composition of observed attachments was mainly the MgO-Al₂O₃ spinel with a trace of calcium. They were solid at casting temperature, easily leading to the nozzle clogging during the casting process. Several iron particles were observed among the attachments. The attachments at the bottom of the SEN were the polyhedral spinel particles contained by CaO-Al₂O₃ phases in Figure 2c. The CaO content of the attachments at the bottom of SEN was obviously higher than that on the inside wall of the SEN, which was mainly from the filled mold flux during the lifting of the SEN after the CC process. Thus, the attachment samples on the inside wall of the SEN at positions 1 and 2 can truly reflect the MgO-Al₂O₃ spinel clogging behavior of the SEN during the CC process of Al-killed Ca-treated Steel. The composition of clogging materials was analyzed using SEM-EDX. More than 200 positions in samples 1 and 2 were measured. The compositions were plotted in the MgO-CaO-Al₂O₃ ternary diagram, as shown in Figure 3. Most of the attachments were Al_2O_3 and MgO- Al_2O_3 with the high melting temperature. The percentage of full liquid attachments at the casting temperature of 1796 K was less than 5%, indicating an extremely low probability of nozzle clogging. The crystallization of solid spinel phases in the CaO-Al₂O₃-MgO may lead to a small change of the liquid-based phase composition [32,33]. Thus, solid inclusions were responsible for the clogging of SEN during the CC process.

To further identify the clogging mechanism of the SEN, a sample was taken in position 4. After mounting, polishing, and Pt coating, the composition distribution of the cross-section sample from the clogging surface to the nozzle matrix was analyzed by elemental mapping, as shown in Figure 4. The composition of the nozzle matrix was alumina. There was a 3–5 mm Al₂O₃-rich Al₂O₃-MgO-CaO clogging material layer attached on the inside wall of the SEN. Reactions with SEM material and steel/inclusions was hardly detected. Thus, the nozzle clogging was caused by the attachment of inclusions on the nozzle inside wall. It was observed that many solidified iron particles were distributed in the clogging layer. Notably, there was a line of iron particles on the nozzle/attachment interface, indicating that the molten steel solidified on the inside wall at the casting start due to the lower initial

temperature of the SEN than the molten steel. The formed solidifying iron particles on the surface of the nozzle gave rise to the capture of the solid inclusion particles at the casting start. During the steady casting process, inclusions with high melting temperature continuously attached on the nozzle inside wall, leading to the clogging of SEN.



Figure 2. Morphology and composition of clogging materials at various positions of the SEN: (a) position 1, (b) position 2, (c) position 3.



Figure 3. Composition distribution of clogging materials.



Figure 4. Materials composition from inside wall of the SEN contacting the flowing molten steel to the original matrix of the SEN.

4. Inclusions in the Steel

After the calcium treatment of the molten steel, inclusions were modified to liquid CaO-Al₂O₃-MgO at the steelmaking temperature. As shown in Figure 5, most of the CaO-Al₂O₃-MgO inclusions were liquid at 1796 K. There were some inclusions located out of the liquidus at 1796 K due to their higher contents of Al₂O₃ and MgO. Figure 6 shows the elemental mapping of typical inclusions in the molten steel in the tundish. As shown in Figure 6a, the inclusion was spherical, indicating that it was full liquid in the molten steel. In Figure 6b, the inclusion was nearly spherical since it was a partial liquid inclusion consisting of a liquid CaO-Al₂O₃ phase and solid MgO-Al₂O₃ phases at the casting temperature. The harmful solid CaS was hardly detected in the current steel due to insufficient T.Ca in the molten steel and the rapid cooling rate of the molten steel sample by quenching. It was concluded that most of the inclusions were liquid in tundish at the casting temperature, which can hardly cause the clogging of SEN. Even the number of the solid and the partial liquid inclusions were low, while they may be the key factor leading to the nozzle clogging.



Figure 5. Composition distribution of inclusions in the molten steel of the CC tundish.



Figure 6. Elemental mapping of typical inclusions in the steel. (**a**) pure phase inclusion, (**b**) multiphase inclusion.

5. Inclusion Liquid Fraction and Clogging Possibility

To investigate the relationship between the liquid fraction and clogging possibility of inclusions, the liquid fraction of each inclusion and clogging particle was calculated using FactSage thermodynamic software (7.1, FactSage, Montreal, QC, Canada) with the database of FToxid. Figure 7 shows the composition and liquid fraction of clogging materials and inclusions. The liquid fraction of the CaO-Al₂O₃-MgO phase was significantly influenced by the ratio of CaO/(MgO + Al₂O₃). Clogging materials were mainly MgO-Al₂O₃ with less than 20% liquid phases. On the contrary, most of the inclusions were full liquid CaO-Al₂O₃-MgO in tundish at the casting temperature. The percentage of MgO-Al₂O₃-rich solid inclusions were very low. The frequency of liquid fraction of clogging materials and inclusions was shown in Figure 8. The roughly 70% clogging materials were pure solid. The percentage of full liquid inclusions was 60%, and the percentage of inclusions with a liquid fraction of higher than 50% was over 85%. It should be noted that the percentage of inclusions with a liquid fraction of less than 10% was under 5%. To investigate the nozzle clogging possibility caused by inclusions with various liquid fractions, the ratio of clogging materials and inclusions with the same liquid fraction range in Figures 7 and 8 was calculated and normalized, as given in Equation (1). The evaluated nozzle clogging possibility of inclusions is shown in Figure 9. The "=0" and "=100" represent that the liquid fraction is 0 and 100%, respectively. With the increase of the liquid fraction of inclusions, the nozzle clogging possibility obviously decreased. It was indicated that the nozzle clogging was mainly caused by inclusions containing less than 20% liquid phase.

$$P^{j} = \frac{f_{c}^{j} / f_{i}^{j}}{\sum_{i=1}^{n} f_{c}^{j} / f_{i}^{j}}$$
(1)

where P^{j} is the nozzle clogging possibility of inclusions with a liquid fraction range *j*, and f_{c}^{j} and f_{i}^{j} are percentages of clogging materials and inclusions in a liquid fraction range *j*, respectively.



Figure 7. Composition and liquid fraction of clogging materials of the SEN and inclusions in the steel: (a) clogging materials, (b) inclusions in the steel.



Figure 8. Frequency of the liquid fraction of clogging materials of the SEN and inclusions in the steel.



Figure 9. The dependence of SEN clogging possibility on the liquid fraction of inclusions.

The nozzle clogging behavior was closed to the wettability between inclusion, steel, and nozzle. An inclusion is stably attached on the inside wall of the nozzle when the free energy change for the attachment of the inclusion on the nozzle refractory is negative, as can be determined from Equation (2) [34]. The interface tension between the inclusion and nozzle can be expressed as surface tensions of the inclusion and nozzle in Equation (3). Expressions of surface tensions of the inclusion and nozzle are derived as Equations (4) and (5) according to Young's equation [35]. Substituting Equations (3)–(5) into Equation (2), the term of attachment of the inclusion on the nozzle wall is obtained as the function of contact angles of nozzle-steel and inclusion-steel Equation (6). The schematic of attachment mechanism of an inclusion to the nozzle wall is shown in Figure 10. The smaller θ_{N-S} and θ_{I-S} benefit the flow of the molten steel between the nozzle wall and the inclusions, while the larger θ_{N-S} and θ_{I-S} promote the adhesion of the inclusion on the nozzle refractory. Figure 11 shows the contact angle between CaO-Al₂O₃-MgO inclusions and the molten steel. The data was summarized from published literatures [34,36–43]. The relationship between contact angle and the mass fraction of CaO in CaO-Al₂O₃-MgO inclusions was fitted as Equation (7). Meanwhile, liquid fractions of CaO-Al₂O₃-MgO inclusions at 1873 K and 1796 K were calculated using FactSage software. The contact angle of Al₂O₃, MgO, or MgO-Al₂O₃ with the molten steel is larger than 120°. Calcium aluminates with less than 20% CaO are pure solid at steelmaking and casting temperatures. With the CaO content in CaO-Al₂O₃-MgO inclusions increased to 20%, the contact angle between inclusion and steel is still larger than 110°, indicating the higher clogging possibility of solid inclusions. The contact angle between CaO-Al₂O₃-MgO inclusions with 35–60% CaO and the molten steel obviously decreased to 50° – 80° since they are partially or fully liquid at 1873 K. The contact angle between the pure solid CaO inclusion and the molten steel goes back to 110°–135°. Thus, solid inclusions more easily attach on the nozzle wall than liquid inclusions. As shown in Figure 11, the contact angle between inclusion and steel is roughly in inverse proportion to the liquid fraction of inclusions. In the current study, θ_{N-S} can be assumed to be a fixed value since the same Al₂O₃-based SEN used during the CC process. It is inferred from Equation (7) that there is a critical value of θ_{LS} for the inclusion attachment on the nozzle. Thus, the contact angles of solid inclusion–steel and liquid inclusion–steel are larger than 110° and smaller than 80°. The contact angle between inclusion and steel is roughly in inverse proportion to the liquid fraction of inclusions. Thus, there is a critical value of liquid fraction of inclusions causing the nozzle clogging as the observed results in Figure 9.

$$\Delta G = \gamma_{I-N} - \gamma_{N-S} - \gamma_{I-S} < 0 \tag{2}$$

$$\gamma_{I-N} = \gamma_N + \gamma_I \tag{3}$$

$$\gamma_N = \gamma_S \cos \theta_{N-S} + \gamma_{N-S} \tag{4}$$

$$\gamma_I = \gamma_S \cos \theta_{I-S} + \gamma_{I-S} \tag{5}$$

$$\cos\theta_{N-S} + \cos\theta_{I-S} < 0 \tag{6}$$

$$\theta_{I-S} = 134 - 2.6w(\text{CaO}) + 0.024w(\text{CaO})^2 \tag{7}$$

where γ_{N-S} is the interface tension between the nozzle and steel, N/m; γ_{I-S} is the interface tension between the inclusion and steel, N/m; γ_{I-N} is the interface tension between the inclusion and nozzle, N/m; γ_S and γ_I are the surface tension of the steel and inclusion, respectively, N/m; θ_{N-S} is the contact angle between the nozzle and steel, °; θ_{I-S} is the contact angle between the inclusion and steel, °; w(CaO) is the mass fraction of CaO in the inclusion, %.



Figure 10. Schematic of attachment mechanism of an inclusion to the nozzle wall.



Figure 11. Contact angle between CaO-Al₂O₃-MgO inclusions and the molten steel.

Based on the steel composition listed in Table 1, the modification of inclusions in steels with various T.Ca concentration at 1796 K was calculated using FactSage thermodynamic software with the databases of FactPS, FToxid, and FTmisc, as shown in Figure 12a. With the increase of T.Ca content in steel, the evolution route of inclusions was MgO-Al₂O₃→liquid CaO-Al₂O₃-MgO→CaS and CaO. The insufficient Ca injection can hardly fully modify MgO-Al₂O₃ spinel inclusions while

excess T.Ca concentration led to the formation of solid CaS and CaO. There was a 100% liquid zone of inclusions with a narrow T.Ca concentration range of 10–14 ppm, which can hardly lead to the clogging of the SEN during the casting process. However, it was found that inclusions containing more than 20% liquid phase also can effectively avoid the nozzle clogging in the current casting condition. Thus, the appropriate T.Ca concentration range can be enlarged to 4–38 ppm. Figure 12b shows the effect of temperature on inclusion transformation using FactSage thermodynamic software with the databases of FactPS, FToxid, and FSstel. With the decreased of temperature from 1800 K to 1000 K, the evolution route of inclusions in the Al-killed Ca-treated steel was liquid inclusion \rightarrow CaS + MgO-Al₂O₃ \rightarrow CaO-Al₂O₃ \rightarrow 2CaO-Al₂O₃ \rightarrow CaO-2MgO-8Al₂O₃. The liquid fraction of inclusions is sensitive with the tundish temperature. Figure 13 shows the effect of T.O, T.S, and T.Al on the needed T.Ca for the liquid zone of inclusions in Al-killed Ca-treated steels. The 100% and 20% liquid zones for Ca treatment increased while the 20% liquid zone for Ca treatment increased.



Figure 12. Transformation of inclusions in the Al-killed Ca-treated steel with various calcium concentration and temperature. (**a**) effect of calcium concentration, (**b**) effect of temperature.



Figure 13. Effect of T.O, T.S, and T.Al on the liquid zone of inclusions for Ca treatment. (**a**) T.O, (**b**) T.S, (**c**) T.Al

6. Conclusions

In the current study, the nozzle clogging behavior and inclusion composition in Al-killed Ca-treated steels were observed to investigate the relationship between the liquid fraction of inclusions and the clogging possibility of the submerged entry nozzle.

(1) The clogging materials were mainly MgO-Al₂O₃-rich phases with a liquid fraction of less than 20%, while most of the inclusions were full liquid CaO-Al₂O₃-MgO in tundish at the casting temperature. The nozzle clogging was mainly caused by inclusions containing less than 20% liquid phase under the current casting condition.

(2) The relationship between contact angle and the mass fraction of CaO in CaO-Al₂O₃-MgO inclusions was fitted as $\theta_{I-S} = 134 - 2.6w(\text{CaO}) + 0.024w(\text{CaO})^2$. The critical condition of the inclusion attachment on the nozzle wall was a function of contact angles of nozzle–steel and inclusion–steel as $\cos \theta_{N-S} + \cos \theta_{I-S} < 0$. It was calculated that solid inclusions more easily attach on the nozzle wall than liquid inclusions. It was proposed that there was a critical value of liquid fraction of inclusions causing the nozzle clogging.

(3) To avoid the clogging of SEN by solid inclusions under the current casting condition, the appropriate T.Ca concentration range in Al-killed Ca-treated steels can be enlarged from the 100% liquid inclusion zone of 10–14 ppm to 20% liquid inclusion zone of 4–38 ppm. The 20% liquid zones for Ca treatment increased with a higher T.O in steel, while it was enlarged with with the increase of the T.S and T.Al.

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