Three-Dimensional Evaluation of Inclusions during the Production of Stainless Steel

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Abstract: Nozzle clogging is a serious problem during continuous casting in the steel industry. The present work is focused on a comparison of the inclusion characteristics in two similar steel grades of high-silicon non-calcium treated (HSiNC) stainless steels with respect to clogging during continuous casting. During two plant trials (Non-clogged heat: Fe-19Cr-12Ni-2Si, Clogged heat: Fe-23Cr-19Ni-3Si), samples of liquid steel and slag were taken during different stages of the ladle treatment and casting. After electrolytic extraction of the steel samples, characteristics of inclusions and clusters (such as morphology, composition, size and number) were investigated in three dimensions (3D) on the surface of film filter with an open pore size of 1 μm by SEM in combination with EDS. It was found that all the steel samples of both heats contain spherical (SP), irregular and regular (IR) inclusions and clusters (CL). The morphology and composition of inclusions and clusters in both heats are changed during the ladle treatment and casting. In the Non-clogged heat, the composition was mostly MgO-SiO_2-Al_2O_3-CaO (with lower concentration of Al_2O_3). In the Clogged heat, the compositions of IR inclusions and clusters were mostly MgO-Al_2O_3 spinel (with higher concentration of Al_2O_3) and the complex SP inclusions contained Al_2O_3-MgO-CaO-SiO_2. The compositions of inclusions and clusters were studied as functions of size and morphology.

Keywords: stainless steel, inclusion, cluster, morphology, composition, clogging

1. Introduction

Nozzle clogging is a serious problem during continuous casting in the steel industry. Clogs in the nozzle change the nozzle flow pattern, disrupt the flow in the mould, and result in top slag entrainment and surface defects[1]. Clogging problems caused by spinel inclusions have been reported by some researchers. Park et al. [2] and Sakata[3] pointed out that the spinel inclusions tended to adhere on the nozzle wall. Therefore, the control of the soluble Al and Mg content in molten steel is very important to inhibit spinel formation and nozzle clogging during casting.

A mechanism for formation of spinel inclusions in stainless steel is discussed based on a thermodynamic consideration of molten steels[4-9] and slag composition[10-13]. The formation of spinel inclusions was considered to be due to a formation of singular spinel (only consisting of $MgO\cdot Al_2O_3$) and due to crystallization of spinel from liquid droplets of CaO-SiO_2-MgO-Al_2O_3[2] during solidification. Park[7] reported that the inclusions containing the $MgO\cdot Al_2O_3$ crystals were not observed in Fe-16Cr-14Ni if the concentration of Al_2O_3 in the inclusions was smaller than 20mass%. However, the number of those inclusions increased drastically at Al_2O_3 concentrations larger than 20mass%. Todoroki and Mizuno[12] found that an increased silica content in the slag can enhance the formation of spinel inclusions in Fe-18Cr-8Ni steels. Furthermore, the effect of ferrosilicon additions on the composition of inclusions was also reported[14-16]. For instance, Park and Kang[14] reported that the use of FeSi with a low aluminum content could suppress the formation of Al_2O_3 in the inclusions, while the addition of FeSi with a higher Al content promoted an increase of Al_2O_3 in the inclusions and a formation of spinel. However, various specific conditions and technological parameters of steel production can strongly influence the formation of spinel inclusions in different steel grades.

In the present study, the inclusion characteristics (such as morphology, number, size and composition) relating to a clogging problem were investigated in two high-silicon non-calcium treated (HSiNC) stainless steels. The characteristics of inclusions and clusters in steel samples taken during ladle treatment and casting were compared for non-clogged and clogged heats. The differences of inclusions and clusters on different stages of production of analyzed steel grades were discussed as possible reasons of nozzle clogging during casting.

2. Experimental

2.1 Sample Preparation

In this study, two similar steel grades of high-silicon non-calcium treated (HSiNC) stainless steels were investigated regarding clogging during continuous casting. During actual steel production an Fe-23Cr-19Ni-3Si steel grade (denoted as a Clogged steel) has a much higher possibility for nozzle clogging in comparison to an Fe-19Cr-12Ni-2Si steel grade (denoted as a Non-clogged steel). The content of the main elements in these two steel grades is given in Table 1. Plant heats (70-75 ton) of both steels were done in a scrap-based steel plant. The main alloying of liquid steel by FeSi was carried out in both heats at the final stage in an AOD converter. Thereafter, the chemical composition of liquid steel was corrected during ladle treatment by additions of some amounts of FeSi and other alloys. Samples of liquid steel were taken from the ladle and tundish by using lollipop samplers (12 mm thickness) with Ar protection during the first and final stages of ladle treatment and casting, as shown schematically in Figure 1. Furthermore, slag samples were taken by scoop-type samplers at the same times.

Table 1 Content of main elements in steels

Steel	Content of elements (mass%)									
	C	Si	Cr	Ni	Mn	Mo	P	S	N	Al
Non-clogged	0.05	1.90	19.00	11.70	1.15	0.14	0.022	0.0011	0.025	0.003
Clogged	0.02	2.68	23.36	19.16	1.72	0.26	0.024	0.0006	0.043	0.003

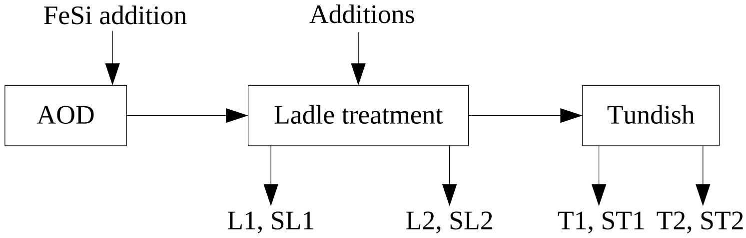


Fig. 1 Schematic illustration of sampling of liquid steel and slag

2.2 Investigation of inclusions and clusters

To investigate inclusions and clusters in steel after electrolytic extraction (EE) in three dimensions, a specimen (13×9×3 mm) was cut out from the central part of a vertical slice from each steel sample. A galvanostatic electrolytic extraction of inclusions from metal specimens was carried out using a 10% AA (10 v/v% acetylacetone - 1 w/v% tetramethylammonium chloride - methanol) and a 2% TEA (2 v/v% triethanol amine - 1 w/v% tetramethylammonium chloride - methanol) non-aqueous solution. The current density during the EE was 35-45 mA/cm^2. Total weight of dissolved metal during electrolytic extraction was varied in the range 0.08-0.10 g. In this case, a thickness of dissolved layer of metal specimen was in the range 90-110 µm. The solution containing inclusions and clusters after electrolytic extraction was filtrated through a polycarbonate (PC) film filter membrane with an open pore size of 1 µm. The characteristics (such as morphology, size and number) of extracted inclusions and clusters were investigated on a surface of film filters by using a scanning electron microscope (SEM). The composition of inclusions was determined by energy dispersive spectroscopy (EDS). The composition of inclusion and clusters was normalized with respect to the MgO, Al_2O_3, SiO_2 and CaO contents. Furthermore, the compositions of inclusions and clusters obtained by 3D investigations after electrolytic extraction were compared with results obtained by conventional two-dimensional (2D) observations of inclusions on polished cross sections of steel samples.

The spatial diameter (d_V) of each inclusion or cluster was determined by using WinROOF software as the equivalent diameter of a circle which has the same area with area of analyzed inclusion or cluster on SEM photographs. Moreover, a circularity factor (*CF*) for each image of inclusion or cluster on photo, which corresponds with morphology of inclusion, was determined by WinROOF according to the following equation:

$$CF_i = 4\pi \cdot \frac{A_i}{P_i^2} \qquad (1)$$

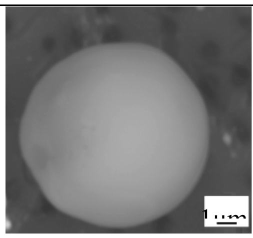
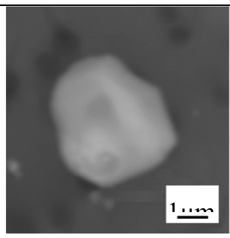
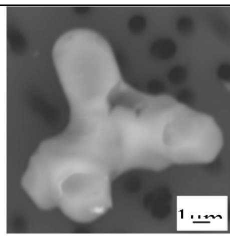
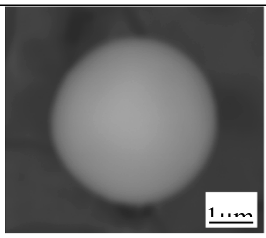
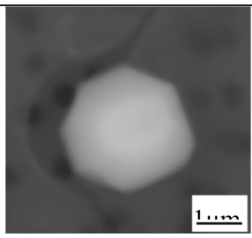
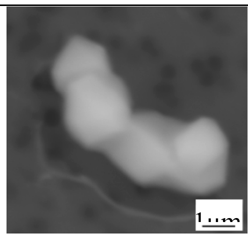
where A_i and P_i are the area and perimeter of *i*-th inclusion image on SEM photograph determined by WinROOF software. In this study, the *CF* value was used for estimation of morphology of observed inclusions and clusters in steel samples.

3. Results and Discussion

3.1 Classification of inclusions

In the present study, inclusions in all steel samples of Non-clogged and Clogged heats were classified into three different groups based on the morphology: Spherical (SP), irregular and regular (IR) and clusters (CL). The typical SEM photographs, size range, *CF* values and composition for different types of observed inclusions are shown in Table 2.

Table 2 Classification of inclusions in steel samples of Non-Clogged and Clogged heats

Heat	Shape	Spherical (SP)	Irregular and Regular (IR)	Cluster (CL)
Non-clogged heat	Typical photo			
	Size range (µm) Circularity factor Composition	1.0 - 10.0 0.90 - 0.97 MgO-SiO_2-Al_2O_3-CaO	2.5 - 10.5 0.70 - 0.92 MgO-Al_2O_3-SiO_2-CaO	4.5 - 10.0 0.50 - 0.70 MgO-Al_2O_3-SiO_2-CaO
Clogged heat	Typical photo			
	Size range (µm) Circularity factor Composition	0.7 - 4.5 0.90 - 0.97 Al_2O_3-SiO_2-MgO-CaO	1.5 - 5.5 0.80 - 0.92 Al_2O_3-MgO-SiO_2-CaO	3.0 - 11.5 0.35 - 0.80 Al_2O_3-MgO-SiO_2-CaO

It can be seen in Table 2 that the size ranges of SP and IR inclusions in the Non-clogged heat is significantly wider (1.0-10.5 µm) than those in the Clogged heat (0.7-5.5 µm), particularly for large size inclusions. However, the size range for clusters in both heats is almost similar. The values of the circularity factor for different types of inclusions in all steel samples varied in the following ranges: 0.90 - 0.97 for SP, 0.70 - 0.92 for IR inclusions and 0.35 - 0.80 for clusters. Though some ranges of *CF* are overlapped, the circularity factor was used for estimation of morphology type for most of inclusions and clusters in this study.

It should be mentioned that the composition of inclusions was list in a descending order based on the oxides content. A subsequent comparison of the inclusion characteristics at different stages of ladle treatment and casting of these steel grades as well as a discussion regarding a potential nozzle clogging problem is done based on this classification.

3.2 Morphology and size of inclusions

In this study, it was found that the morphology of inclusions in Non-clogged and Clogged heats are significantly changed during ladle treatment and casting. Figure 2 shows a relationship between the frequency of inclusions with different morphology in steel samples and the sampling moment. The L1, L2, T1 and T2 samples correspond to different stages of ladle treatment and casting (as shown in Fig. 1). As can be seen in Fig. 2a, the frequency of clusters and IR inclusions in the Non-clogged heat decreases drastically during ladle treatment from 16% CL and 40% IR in L1 sample till 1-2% CL and 1-2% IR in T1and T2 samples. The frequency of spherical inclusions in this steel grade increased and attained to 96-98% in the cast steel (samples T1 and T2). This fact can be explained by the removal of some clusters and by a gradual transformation of most clusters and IR inclusions to spherical inclusions. A spheroidizing of CL and IR inclusions can probably be explained by the changing of inclusion composition (wholly or partially on surface) or by precipitation on the surface of the existing solid IR inclusions to form a new liquid oxide layer. It can completely change morphology and behavior of clusters and IR inclusions regarding clogging problem during casting. The composition of inclusions with different morphology will be discussed below.

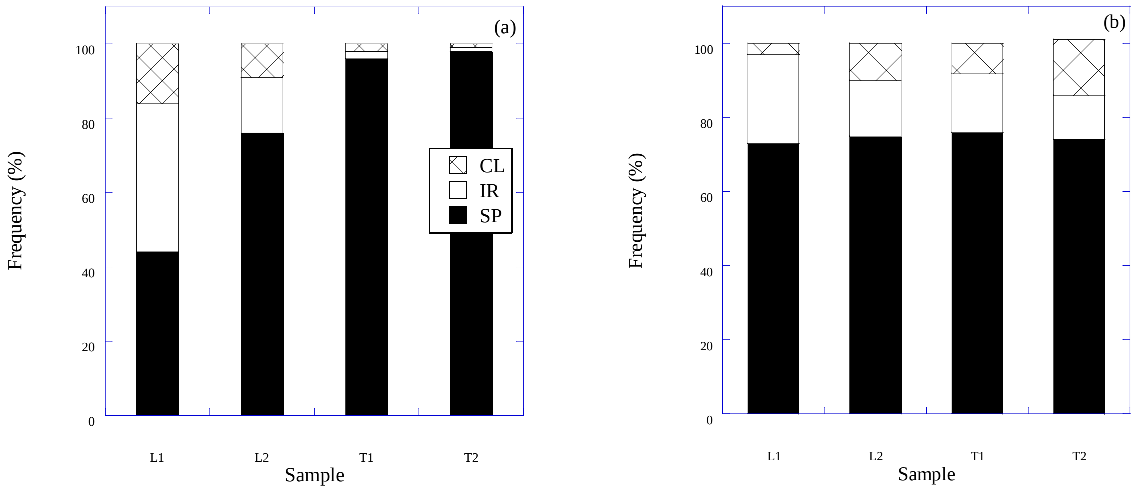


Fig.2. Relationship between morphology of inclusions and sampling moment during ladle treatment and casting of (a) Non-clogged and (b) Clogged heats

As can be seen in Fig. 2b, the frequency of clusters in the steel samples of the Clogged heat increases from 3% (sample L1) to 15% (sample T2) during ladle treatment and casting. Furthermore, the frequency of IR inclusions decreases from 24% to 12%. The frequency of spherical inclusions in steel samples from the Clogged heat is almost stable during all time of ladle treatment and casting (73-76% SP). Based on obtained results, it can be assumed that the clusters in Clogged heat are formed from irregular and regular inclusions during all time of ladle treatment and casting and reached maximum frequency in sample T2 taken from tundish at final stage of casting. Therefore, whereas the morphology of inclusions in Non-clogged and Clogged steels is very similar (see Table 2), it was concluded that the main reasons of nozzle clogging during casting of Clogged heat are the number, size and compositions of clusters and IR inclusions.

It is well known that the large size inclusions and clusters cause more harmful clogging problems and are harmful to properties of final steel product. The frequency of different type of inclusions in Non-clogged and Clogged heats is shown in Fig. 3 as a function of their size. It can be seen in Non-clogged steel (Fig. 3a) that most inclusions in the range of $d_V \geq 4$ μm are spherical (50%) and irregular-regular (31%) inclusions. Only 19% of the observed inclusions in this size range correspond to clusters, which number decreases drastically during ladle treatment of a Non-clogged heat. However, the large size clusters (with $d_V \geq 4$ μm) are dominant (80%) in Clogged steel samples. The frequency of IR and SP inclusions in this size range reaches only 15 and 5%, respectively. Moreover, the inclusions in the range of d_V from 2 to 4 μm in this steel are mostly irregular-regular (45%) inclusions and clusters (35%). Therefore, the large size clusters and IR inclusions in the Clogged heat can be consider as the most possible reason for nozzle clogging problem during casting of this steel grade.

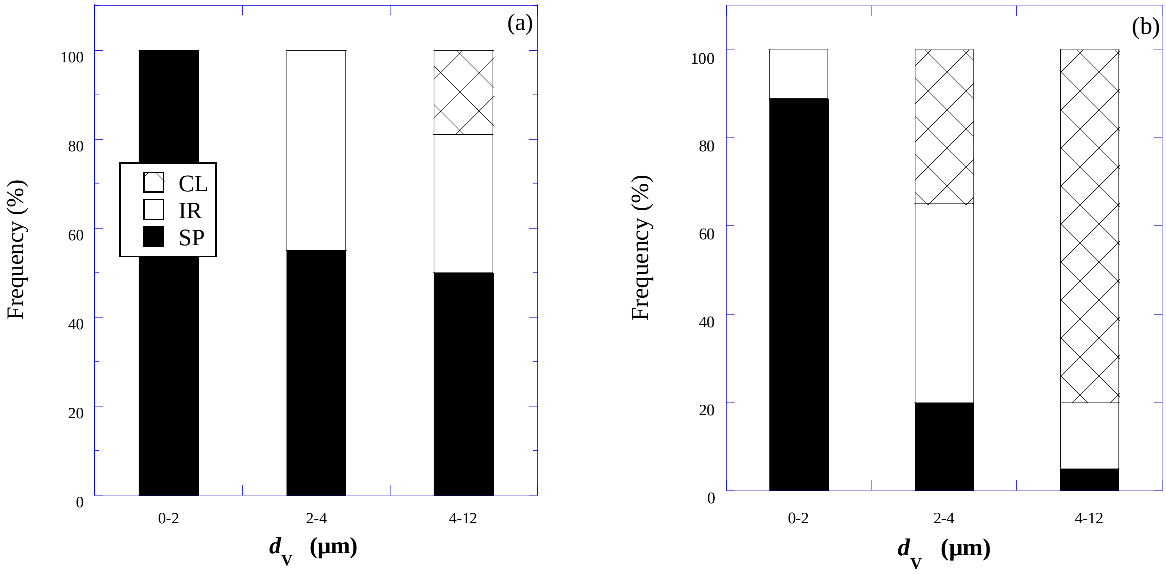
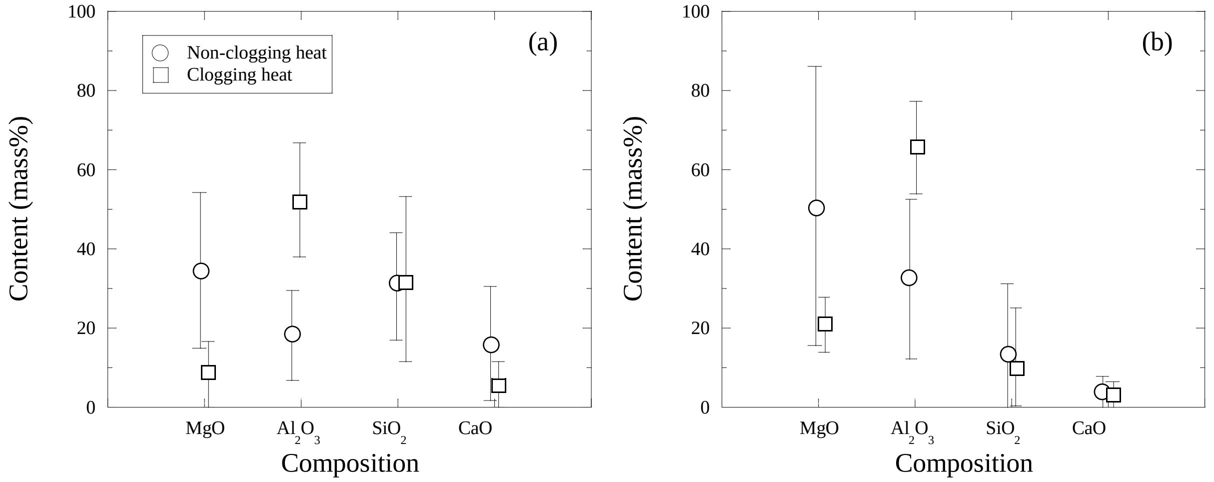


Fig. 3 Relationship between morphology and size of inclusions in steel samples of (a) Non-clogged and (b) Clogged heats

3.3 Composition of inclusions

The average compositions obtained from a 3D investigation of different types of inclusions in Non-clogged and Clogged steels are shown in Fig. 4. Error bars represent the arithmetic standard deviation of the oxide contents in inclusions. It is apparent that in most of the inclusions in the Non-clogged heat the average content of MgO is significantly higher while the Al_2O_3 content is smaller than those in the Clogged heat. The average concentrations of SiO_2 and CaO in inclusions are very similar in both heats. However, the SiO_2 and CaO contents in spherical inclusions in steel samples of both heats are significantly higher than those in IR inclusions and clusters. It may safely be suggested that most spherical inclusions with higher contents of SiO_2 and CaO were liquid (totally or partially) during sampling of steel. Moreover, it can be seen in Fig. 4b and 4c that the compositions of most IR inclusions and clusters in the Clogged heat are very similar.



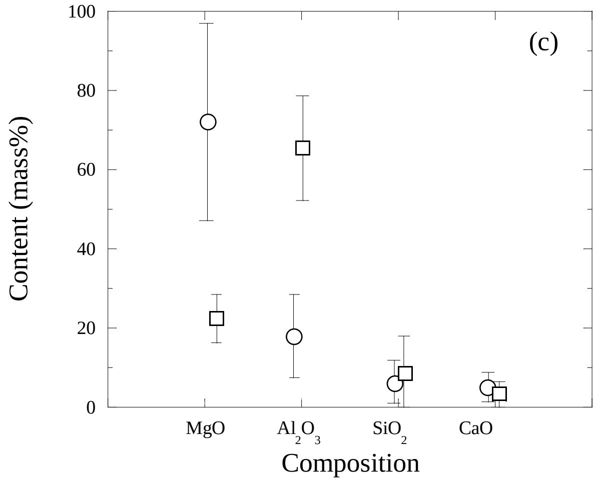


Fig. 4 Average compositions of inclusions in Non-clogged and Clogged heats for (a) Spherical, (b) Irregular-Regular inclusions and (c) Clusters

According to the obtained results (Fig. 2a), 97-98% of inclusions observed in steel samples from tundish (samples T1 and T2) of Non-clogged heat are spherical. Therefore, it is important to investigate the composition of dominant spherical inclusions in this steel. Figure 5 shows a relationship between the composition and spatial size of spherical inclusions in steel samples of Non-clogged heat. The L1, L2, T1 and T2 samples correspond to different stages of ladle treatment and casting (as shown in Fig. 1). It was found that the spherical inclusions smaller than 5 µm have a very scattered composition, particularly in the L1 and L2 samples. For instance, the contents of MgO, Al_2O_3, SiO_2 and CaO in these inclusions are varied in the ranges 4-96%, 2-64%, 1-68% and 0-53%, respectively. Moreover, a dispersion of inclusion composition increases with a decreased inclusion size. However, the spherical inclusions larger than 5 µm have a more stable composition (36-50% MgO, 8-16% Al_2O_3, 24-38% SiO_2 and 4-26% CaO).

It should be pointed out that, though the composition of the observed SP inclusions with d_V > 5µm is more stable, it disagrees significantly with a slag composition in the ladle and tundish. For instance, the contents of MgO, SiO_2 and Al_2O_3 in spherical inclusions are considerable higher, but the CaO content is drastically lower than those in the ladle and tundish slag samples.

It was found that the content of Al_2O_3 in most SP and IR inclusions and clusters in Non-clogged heat is smaller than 20%. Based on the thermodynamic consideration of ternary phase diagram for MgO-Al_2O_3-SiO_2, it was concluded that the formation of $MgO \cdot Al_2O_3$ phase in such inclusions is problematic. As a result, the spinel inclusions and clusters (a main reason of nozzle clogging during casting) were hardly observed in the steel samples from the Non-clogged heat. A similar experimental results obtained by investigation of inclusions in Fe-16%Cr-14%Ni stainless steel grades was reported by Park[7]. Therefore, the content of Al_2O_3 in inclusions can be considered as an important factor in the formation of $MgO \cdot Al_2O_3$ inclusions.

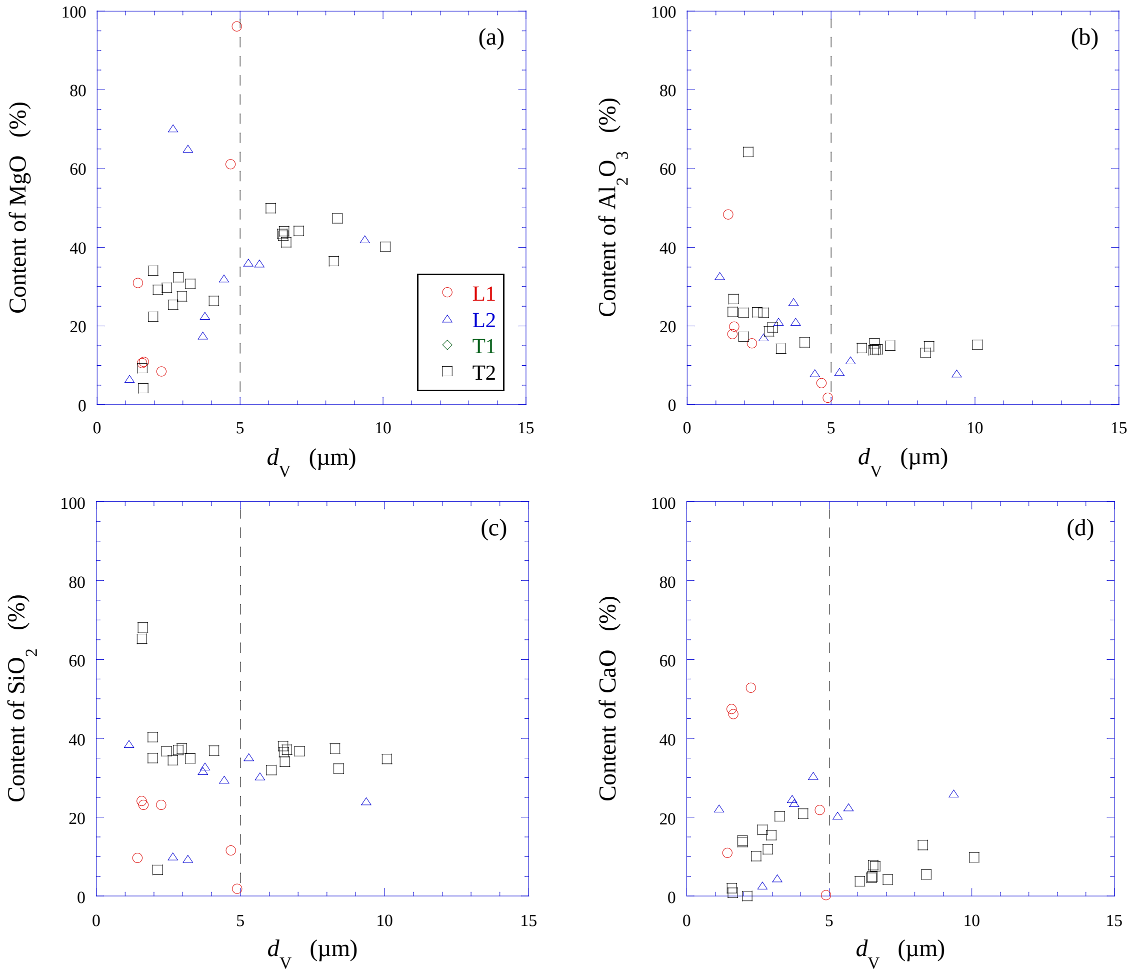
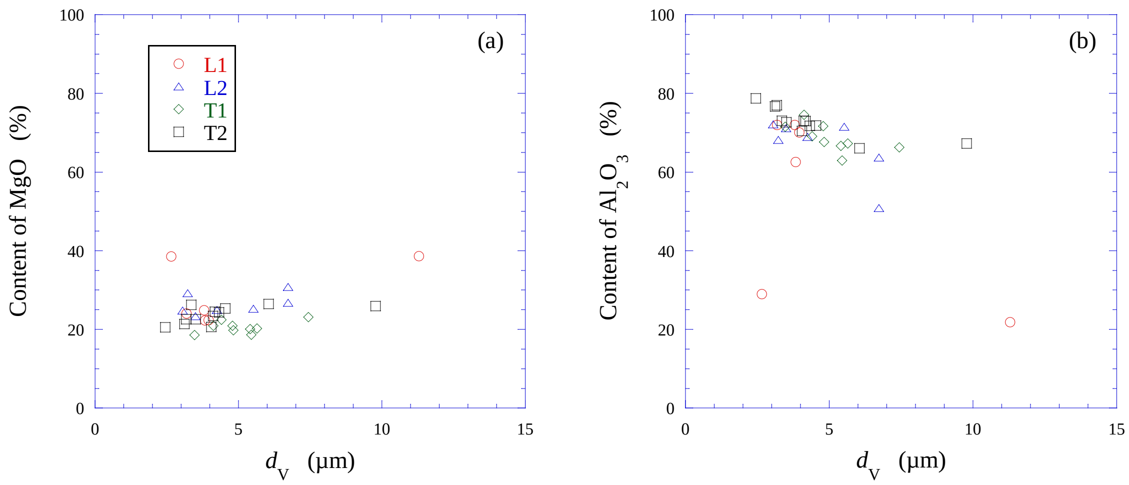


Fig. 5 Composition of spherical inclusions in steel samples of Non-clogged heat



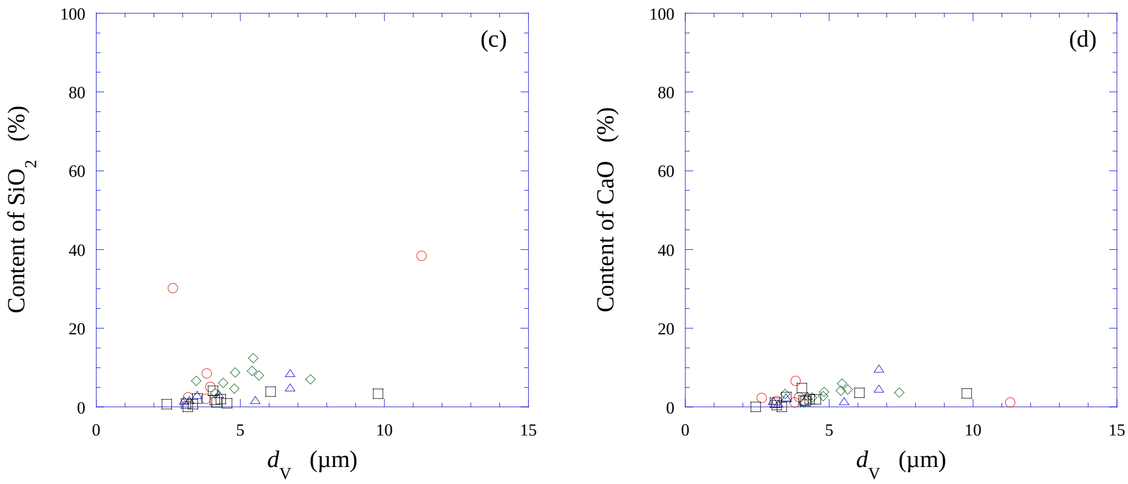


Fig. 6 Composition of clusters in steel samples of Clogged heat

In previous publications [2-3] it was reported that the spinel ($MgO{\cdot}Al_2O_3$) particles and clusters are often responsible for clogging of nozzles during casting. Therefore, though the dominant inclusions in Clogged steel are spherical (73-76%), the present study was especially focused on an analysis of irregular and regular inclusions and clusters. It was shown in Fig. 2b that the number of IR inclusions and clusters in steel samples is kept sufficiently large during ladle treatment and casting (24-27% in T1 and T2 samples). Moreover, the frequency of clusters increases with an increased time of steel treatment and casting (from L1 to T2 samples). Based on investigations of the inclusion composition, it was found that the IR inclusions and clusters in Clogged steel have very similar compositions. Furthermore, that they correspond mostly to $MgO{\cdot}Al_2O_3$ inclusions with low concentrations of SiO_2 and CaO. Figure 6 shows a relationship between the composition and size of clusters in the steel samples of the Clogged heat. It can be seen that most clusters in samples L2, T1 and T2 have almost a stable content of MgO (19-30%) independently of cluster size. However, the concentration of Al_2O_3 in clusters tends to decrease from 60-78% to 50-70% with an increased d_V value, whereas the concentration of SiO_2 and CaO tend to increase with an increased size.

It is interesting to note that the concentration of Al_2O_3 in most clusters of L2, T1 and T2 samples from the Clogged heat is higher than that in pure $MgO{\cdot}Al_2O_3$. This fact can be explained by a higher content of Al in the Clogged steel, particularly in the L2 sample after a correction of the chemical composition of liquid steel in ladle.

The composition of inclusions and clusters obtained from 2D observation on polished cross section of steel samples in most cases are similar with that from 3D investigation on film filter after electrolytic extraction. However, it should be pointed out that the ratio between the MgO and Al_2O_3 contents in the central zone of the large size (>2 µm) IR inclusions and clusters obtained from 2D observations is slightly larger than that from 3D investigation. This may be explained as follows: By 3D investigation of inclusions larger than 2 µm, only a surface layer (approximately 1µm) of inclusions can be analyzed by EDS. Therefore, in the case of 2D observations, the central zones of large size inclusions and clusters can be analyzed more accurately. According to the obtained results, the concentration of MgO in the inclusion center is larger than that in surface layer. However, the Al_2O_3 concentration in the surface layer of IR inclusions and clusters in the steel samples from the

Clogged steel is higher than in the center. The higher concentration of Al_2O_3 in the surface layer of inclusions increases the possibility for clustering of IR inclusions and precipitation on the inner wall surface of the nozzle during casting.

4. Conclusions

Inclusions and clusters were analyzed in steel samples taken at different stages of ladle treatment and casting during production of two high-silicon non-calcium treated (HSiNC) stainless steels (Non-clogged heat Fe-19Cr-12Ni-2Si and Clogged heat Fe-23Cr-19Ni-3Si). The characteristics (such as morphology, size and composition) were investigated in 2D on a polished steel surface and in 3D after electrolytic extraction. The following conclusions were obtained.

1. The frequency of irregular-regular (IR) inclusions and clusters in the Non-clogged steel mostly decreases during ladle treatment. As a result, 96-98% of inclusions in this steel during casting are spherical MgO-SiO_2-CaO-Al_2O_3 inclusions. The spherical inclusions larger than 5 μm have a more stable composition in comparison to the small sized inclusions.

2. The frequency of clusters in the Clogged steel increases to 15% during the ladle treatment and casting, while the frequency of IR inclusions decreases from 24% to 12%. The frequency of spherical inclusions in this steel did not change during ladle treatment and casting. Most of inclusions larger than 4 μm are clusters (80%) and IR inclusions (15%). The composition for most of IR inclusions and clusters in Clogged heat correspond to a $MgO\cdot Al_2O_3$ phase with very small content of SiO_2 and CaO.

3. In the Non-clogged heat, the MgO content in spherical, IR inclusions and clusters is significantly higher and the Al_2O_3 content is smaller than that in the Clogged heat. The SiO_2 and CaO content in spherical inclusions is higher than in IR inclusions and clusters.

4. In the Clogged heat, the Al_2O_3 content in surface layer of IR inclusions and clusters is considerable higher than that in central zone. The higher concentration of Al_2O_3 in surface layer of inclusion increases a possibility for clustering of IR inclusions and clogging of nozzle during casting.

Acknowledgments

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