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Impact of slag refractory lining reactions on the formation of inclusions in steel

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The present study was carried out to investigate the impact of slag refractory lining reactions on the formation of inclusions during ladle treatment of steel. The experiments were conducted on an industrial scale in the ladle at Uddeholm Tooling AB in Hagfors, Sweden. The inclusion chemistry and population during ladle treatment were studied along with the composition of the ladle glaze, taken from the ladle lining. The inclusions in the steel were classified into four groups according to the Swedish standard SS 111116. SEM/EDS analyses were carried out to identify the phases present in both the inclusions and the ladle glaze.

The number of inclusions in the steel before deoxidation was found to increase with the ladle age, i.e. the number of times the ladle had been in use. A similar increase was also found after vacuum degassing and before casting. A great portion of inclusions before casting was found to be supplied by ladle glaze. This observation was further confirmed and explained by thermodynamic analysis. The present results show that ladle glaze is a major source of inclusions in the ladle at Uddeholm Tooling.

Keywords: Slag/ refractory/ lining—reactions, ladle glaze, inclusions, inclusion chemistry, ladle treatment

Introduction

The importance of slag-refractory reactions in ladle treatment has long been realized. A number of efforts[1-5] have been made to study the mechanism and kinetics of the slag-refractory reaction. More and more attention has been paid to the impact of slag-lining reactions on the formation of non-metallic inclusions.[6-15]

Ladle glaze is formed during the draining of a ladle. A film of slag is attached to the ladle walls when the top slag moves down following the steel during casting. The molten slag film adheres and penetrates into the pores of the refractory, forming ladle glaze. When the next heat is poured into the glazed ladle, the glaze layer will be removed or partially removed, resulting in the formation of inclusions in the liquid metal.[6-10]

The present research work is a joint effort of the Division of Metallurgy, Royal Institute of Technology in Stockholm, Sweden, and Uddeholm Tooling AB, Hagfors, Sweden, with the aim of reaching a basic understanding of the effect of ladle glaze on the formation of inclusions based on industrial trial experiments.

Experimental

The industrial trial experiments were carried out in the steel melting shop at Uddeholm Tooling AB in Hagfors, Sweden.

Process description

Uddeholm Tooling is a scrap-based steel mini mill producing tool steels. The process is schematically shown in Figure 1. In an electric arc furnace, 35 to 65 tons of recycled steel are melted. After being treated for phosphorous and carbon, the molten steel is tapped into a ladle and transferred to the ladle furnace station. After deslagging, the steel is deoxidized with aluminium wire or bars and slag formers (alumet, dolomet and lime) are added to form a synthetic slag. Various alloys are added depending on the specification of the steel grade. The melt is heated up to a temperature between 1853 and 1923 K and stirred to ensure homogeneity. Thereafter, the ladle is transferred to a degassing station and placed in a vacuum chamber. During degassing, the steel is stirred by both inductive stirring and gas stirring using argon gas, to eliminate nitrogen and hydrogen from the melt. The vacuum degassing is followed by a floatation period, in which only inductive stirring is used to promote growth and removal of inclusions. Thereafter the refined steel is sent for uphill casting.

Uddeholm Tooling uses two different sizes of ladles, 35 ton and 65 ton. The lining used in the ladles is magnesite (carbon bearing MgO-lining). The lifetime of a ladle lining at Uddeholm Tooling is normally in the range of 25–30 times of usage.

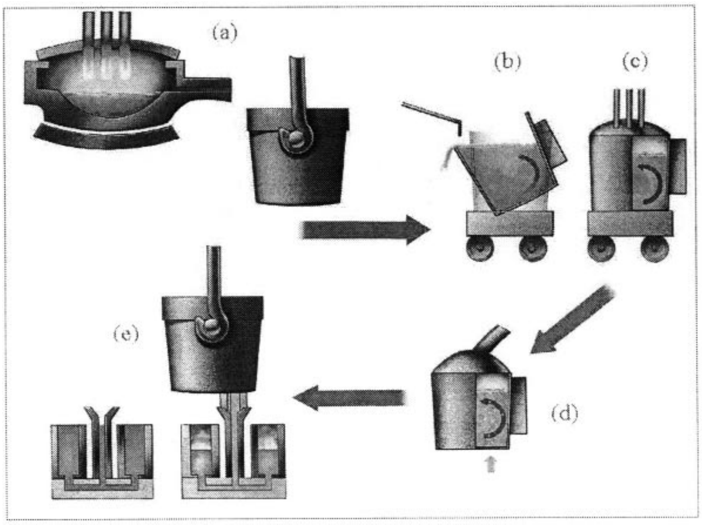

Figure 1. Flow chart of the steel making process at Uddeholm Tooling AB; (a) tapping; (b) deslagging; (c) ladle furnace treatment; (d) vacuum degassing; (e) uphill casting

Sampling

Both steel samples and refractory samples covered with ladle glaze were taken. The steel samples were obtained at different stages of the ladle treatment from four different tool steel grades, following the aging process of the ladles (i.e. the number of times the ladle had been in use). Liquid Solidification Hot Rolling (LSHR) samplers were employed to take the steel samples.[16]

Pieces of the ladle lining covered with glaze were also taken from used ladles of different ages. The samples were taken at different positions in the ladle. These positions are schematically shown in Figure 2.

To understand the slag-refractory reaction, samples of both Electric Arc Furnace (EAF) slag and synthetic ladle slag were taken. The contents of dissolved and total oxygen in the steel melt were also determined.

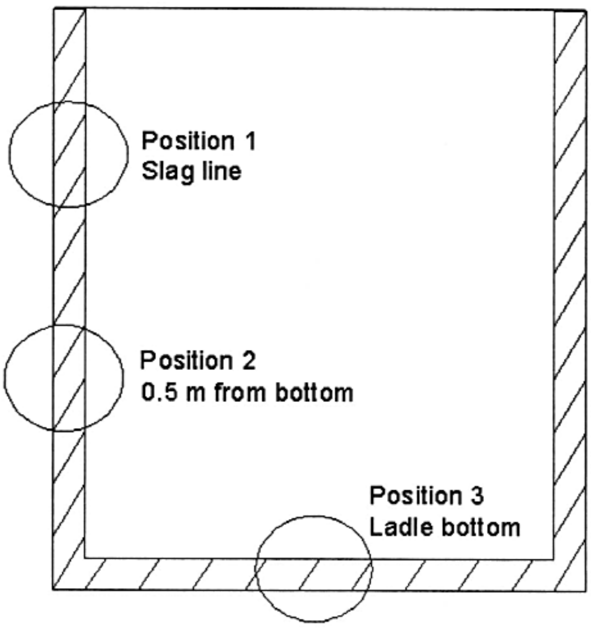

Figure 2. Positions of obtained lining-glaze samples in the ladle furnace

Analysis

Both steel and refractory samples were investigated in an optical microscope, and the inclusions' number and size distribution was evaluated using the Swedish standard SS111116. A JEOL JSM-840 Scanning Microscope attached with an EDS X-ray analyser (Model: Link ISIS series 300, Oxford instruments) was employed to identify the compositions of the phases present in the glaze samples and in the inclusions. For the glaze samples both sections parallel and perpendicular to the surface (in contact with the steel) were prepared.

Results

Inclusion analysis

The steel samples were analysed for inclusion numbers and size distribution. The inclusions found in the samples were classified into four size-ranges, according to the Swedish standard SS111116.[17]

In order to gain knowledge of the number of inclusions flushed off from the glaze layer on the ladle wall during ladle filling, steel samples were taken before aluminium deoxidation. Figure 3 presents the variation in the number of inclusions/mm^2 found before deoxidation as a function of ladle age, for the steel grade ORVAR 2M. The increase in the number of inclusions with increasing ladle age is seen in this figure. Figure 4 shows a similar case for all the steel grades investigated in the current work. Though the process parameters vary considerably with different steel grades, an increase of the number of inclusions with ladle age is well brought out in this figure.

It is particularly interesting to examine whether the ladle age has an effect on the number of inclusions before the melt leaves the ladle. In Figure 5, the numbers of inclusions per area in different size-ranges before uphill casting are plotted against ladle age for the steel grades ORVAR 2M and DIEVAR. While the numbers of inclusions in all size-ranges show an increasing trend, the number of inclusions of the smallest size increases greatly with the ladle age.

Lining-glaze analysis

Glaze-lining samples were taken from two ladles of age 4 and age 18. The ladle of age 18 was in the end of its usage.

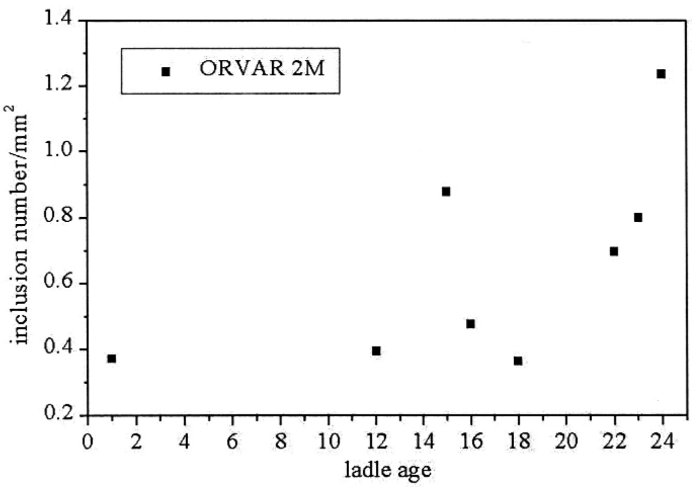

Figure 3. Inclusion population (number/mm^2) as a function of ladle age before aluminium de-oxidation for the steel grade ORVAR 2M

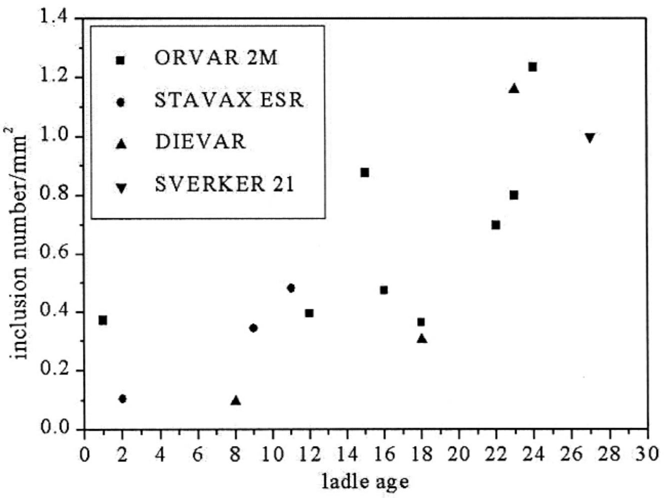

Figure 4. Inclusion population (number/mm²) as a function of ladle age before aluminium deoxidation for all steel grades

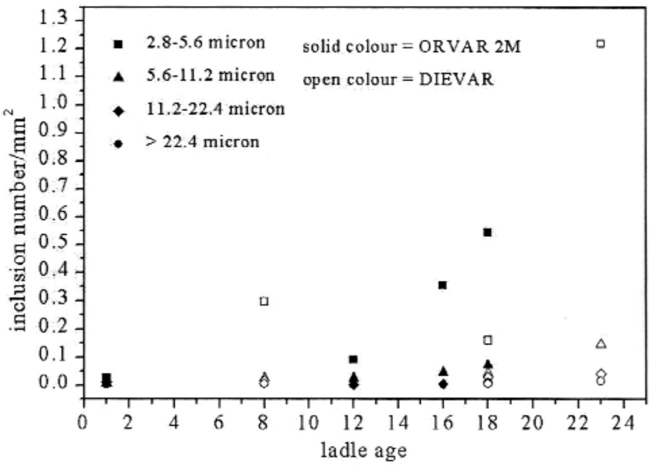

Figure 5. Variation of inclusion population (number/mm²) with ladle age in four different size ranges before uphill casting for the steel grades ORVAR 2M and DIEVAR.

The samples were taken at three different positions, schematically shown in Figure 2:

(1) At the slag line on the side wall

(2) At a position approximately 50 cm from the ladle bottom on the side wall

(3) At the bottom of the ladle

Both the sections parallel to and perpendicular to the glaze surface were examined.

Figure 6a presents the microphotograph of the cross section of a typical lining-glaze sample. In the figure a slag infiltrated layer is seen, covered by an outer layer having many MgO areas of different sizes. It should be pointed out that there is a decarburized refractory layer between the magnesite refractory and the slag infiltrated layer. Because of the difficulties in showing all the layers in one microphotograph with a suitable magnification, these layers are not included in Figure 6a. An ocular examination of the samples also showed that the slag infiltrated zone was much thicker in an older ladle. SEM/EDS analyses indicated that the microstructure of the infiltrating slag was the same as the slag in the outer layer.

Figure 6b was taken with a higher magnification, in the diffuse boundary zone between the outer layer and the slag-infiltrated layer. The dark islands (marked as phase 1) were identified as MgO. Some pores filled with plastic during the preparation of the specimen are also seen. Even some iron drops were found in the samples. It is interesting to note that the original slag consists of two phases, a dark grey phase (marked as phase 2) and a light grey phase (marked as phase 3). The two phases distribute uniformly in each other. In some areas, the dark grey phase appears to be dendrites. The uniform distribution and the existing dendrites strongly suggest that the dark grey phase precipitated from the liquid phase during cooling.

Despite the difference in sampling position and ladle age, all the samples at and below the slag line showed identical phases. Table I lists the results of the EDS analyses of phase 2 and phase 3.

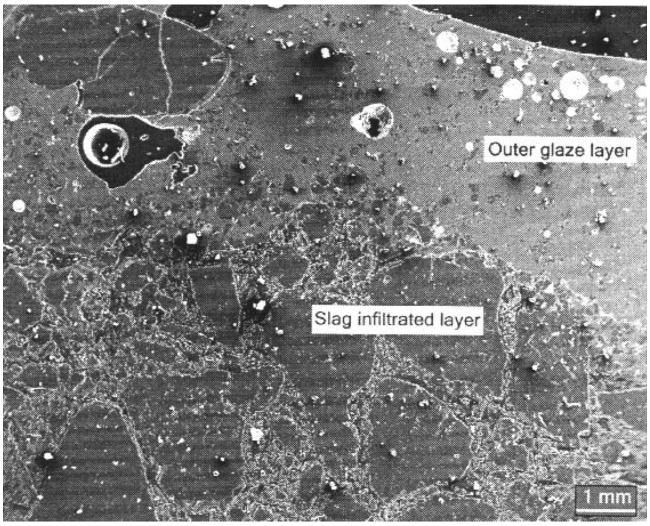

Figure 6a. Cross-section of glaze-lining sample

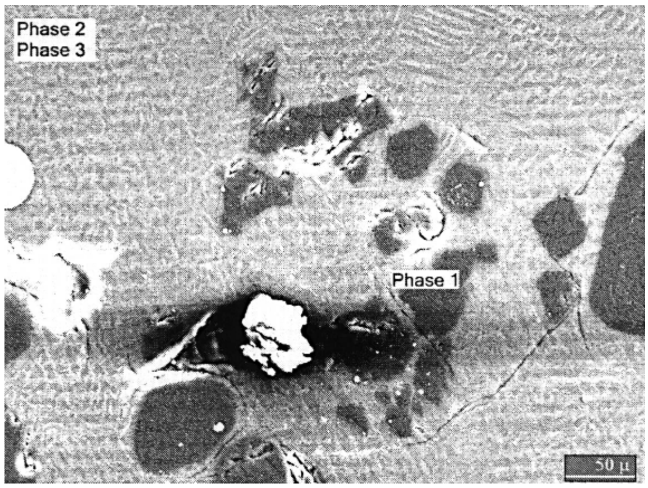

Figure 6b. Microstructure of slag-infiltrated layer with MgO-areas, magnification 500x

Table I
Results of SEM/EDS analyses of phase 2 and 3 in the ladle glaze

Average comp	Sample Age/ pos	Al_2O_3 (wt%)	CaO (wt%)	MgO (wt%)	SiO_2 (wt%)	Analysis points
Phase 2 (dark grey)	4 / 3	41.0	54.3	1.5	2.9	9
	18 / 2	40.1	54.4	2.1	3.0	16
	18 / 3	39.2	53.9	2.0	4.7	4
Overall average	---	40.3	54.3	1.9	3.2	29
Composition range						
Phase 2 (dark grey)	4 / 3	38.8–43.3	52.5–55.9	0.7–2.7	1.9–4.2	9
	18 / 2	38.8–41.1	52.5–53.9	1.2–3.4	1.9–4.8	16
	18 / 3	37.6–40.9	53.7–54.0	1.4–2.7	3.4–5.6	4
Overall comp. range	---	37.6–43.3	52.5–55.9	0.7–3.4	1.9–5.6	29
Average comp						
Phase 3 (light grey)	4 / 3	31.4	45.8	8.5	13.5	8
	18 / 2	32.3	50.2	6.5	10.4	14
	18 / 3	33.6	50.5	6.9	10.3	3
Overall average	---	32.2	48.8	7.2	11.4	25
Composition range						
Phase 3 (light grey)	4 / 3	27.3–37.4	44.1–48.1	1.1–12.1	11.4–14.7	8
	18 / 2	28.9–35.9	46.5–54.8	3.4–9.6	7.2–13.2	14
	18 / 3	28.5–35.6	48.4–49.9	4.1–9.5	11.7–13.4	3
Overall comp. range	---	27.3–37.4	44.1–54.8	1.1–12.1	7.2–14.7	25

Discussion

Ladle glaze is suspected of being a major source of non-metallic inclusions in the steel melt during ladle metallurgy.[11-15] A thin coating of slag is formed when the top slag is in contact and reacts with the ladle lining during the draining of the ladle. This molten slag layer adheres and penetrates into the pores of the refractory, forming the ladle glaze. The adhering and penetration into pores of the refractory can be clearly seen in Figure 6a. When another cast of steel is poured into the ladle, it is expected that the outer layer and parts of the slag infiltrated layer are removed or partially removed from the ladle wall. Parts of this re-melted slag and the non-metallic particles originally kept in the glaze can be retained in the liquid metal as inclusions.[6-10]

The number of inclusions in the melt depends on many factors, such as the temperature of the steel, the slag composition, the steel grade, the manner of deoxidation, the stirring conditions and the ladle age. If the rest of the parameters are kept nearly constant, a plot of the number of inclusions as a function of ladle age would reveal the contribution of inclusions formed by the ladle glaze. As seen in Figure 3, the number of inclusions in steel grade ORVAR 2M shows a clear increasing trend with the ladle age. The increase becomes even more drastic after age 18. In the case of the same steel grade, the operating conditions would not vary considerably. It is reasonable to believe that the difference between the number of inclusions in a newer ladle and the number of inclusions in an older ladle before deoxidation is mainly due to the contribution of the ladle glaze.

As mentioned in the results section, ocular examination of the lining samples showed that the slag-infiltrated layer became thicker and more porous while the ladle became older. The high porosity would in turn enhance the penetration of slag and therefore the slag-refractory reaction. As a result of this reaction, a thicker glaze layer with more tiny solid particles would be formed as a function of the ladle age. This acceleration would lead to the drastic increase in the number of inclusions found in the melt in the older ladles, as shown in Figures 3, 4 and 5.

The difference between the total oxygen content and the dissolved oxygen content in the melt would be the oxygen content associated with oxide inclusions in the steel. In Figure 7 the difference between the total oxygen content in the steel sample and the content of the dissolved oxygen in the melt before uphill casting shows a substantial increase when the ladle is used for more than 12 heats. This result is in good agreement with the results shown in Figure 5.

SEM/EDS analyses of the glaze samples indicated that the microstructure of the infiltrating slag was the same as the slag in the outer layer. As shown in Figure 6b, the dark islands (phase 1) were identified as MgO. The surrounding matrix was found to consist of two phases, a dark grey phase (phase 2) and a light grey phase (phase 3). Table I indicates that phase 2 contains mostly CaO and Al_2O_3, with some small amounts of MgO and SiO_2. The consistency of the chemical composition would suggest that this phase is very likely a compound. Thermodynamic analysis shows that this composition is very close to the composition of the $3CaO{\bullet}Al_2O_3$ compound. In contrast with phase 2, phase 3

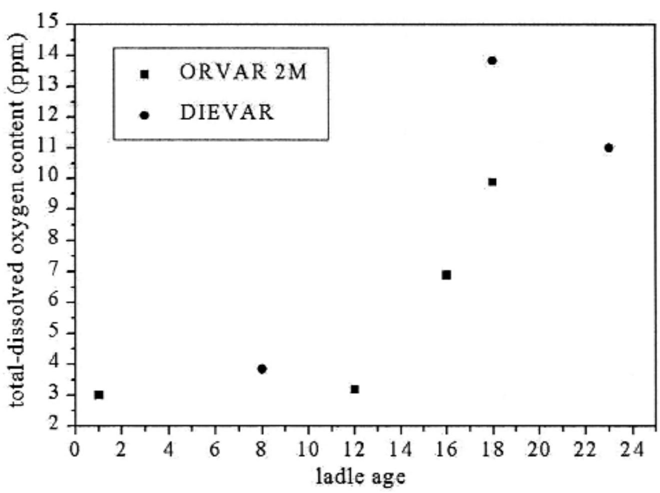

Figure 7. Difference between total and dissolved oxygen contents in the melt before uphill casting as a function of ladle age in the case of steel grades ORVAR 2M and DIEVAR

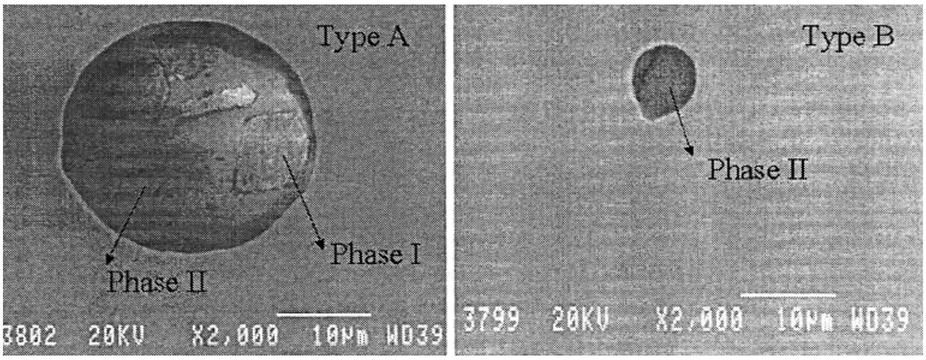

Figure 8. Microscopic photographs of the two inclusions types A and B observed in the steel samples before uphill casting

does not have a narrow composition range. According to the phase diagram of the Al_2O_3-CaO-MgO-SiO_2 system, this phase is a super- cooled liquid.

Only two types of oxide inclusions were found in the steel before casting. Figure 8 presents the microphotographs of the two types of inclusions. In the inclusions of type A, two phases were detected. As seen in the figure, the areas having sharp edges are pure MgO and the matrix has a composition close to $3CaO•Al_2O_3$. The inclusion sizes were around 20 μm. Only one phase was detected in the inclusions of type B, namely an oxide solution containing mostly CaO and Al_2O_3 with low concentrations of MgO and SiO_2. The size of the inclusions of type B was found to vary between 2 μm and 20 μm. The coexistence of MgO pieces and a liquid phase having a composition close to $3CaO•Al_2O_3$ in the inclusions of type A is a clear indication that the A-type are generated by the slag infiltrated zone of the ladle glaze. Even a fraction of the inclusions of type B could have been supplied by the ladle glaze, especially the bigger ones. The small inclusions of type B are expected to be the product of the reaction between $Al_2O_3•MgO$ spinel and dissolved calcium in the melt.[12-15]

The outer layer of the glaze shown in Figure 6a would be removed shortly after the filling of the ladle. The slag-infiltrated layer would then be in direct contact with the liquid steel. The strong gas stirring during the degassing period would provide favourable conditions for the detachment of the tiny pieces of MgO along with the liquid having a composition close to $3CaO•Al_2O_3$, forming inclusions in the melt.

In some steel industries, the degassing period is considerably long. This period is, in some practices, even followed by a period of floatation. The present study shows that while the longer degassing time and the use of a floatation period might increase the probability of separation of inclusions by floatation, they might also increase the rate of detachment of the inclusions of types A and B, especially in an old ladle. An optimization of the degassing time and floatation time, by taking into account of the ladle condition, intensity of stirring, steel grade and its demands on the cleanness of the steel, would be beneficial in view of both energy saving and production cost.

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