State of the Art Control Measures for Aluminium Fade and SEN Clogging during Steelmaking Operations

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Abstract: Crack formation, fatigue failure of components and other process interruptions in liquid steel practices such as ladle nozzle clogging, SEN clogging, break outs are mainly due to residual deoxidation products such as alumina present in steels. The present paper deals with the issues in steel processing operations and provides state-of-the-art control measures for clean steel production. Investigations regarding the residual alumina content and its consequences at integrated steel plant shows that, Al-fade of maximum 0.02% is observed, which produces equivalent of 37 Kg of alumina in the liquid steel. Furthermore, slag carry over, re-oxidation, improper argon rinsing practice, aluminium consumption at secondary steelmaking practices also influences the alumina formation during steelmaking practices. The residual alumina not only affects the quality of steel, but also results in process interruptions such as ladle choking, SEN choking, subsequent break outs etc. various steelmaking practices influences clogging and aluminium fade are discussed and possible suggestions are given to improve the cleanliness of steel.

1. Introduction
Since 1960, secondary steelmaking practices are employed in steel plants for production of quality steels. Secondary steelmaking practices primarily includes argon purging, electric arc heating, vacuum and wire treatment. Deoxidation, desulphurisation, degassing and inclusion control are the refining techniques involved in secondary steelmaking sections to enhance the quality of steels. Though the steel plants are practicing tough control in quality of steel products during steelmaking processes, there is always ample scope to improve it. Production of steel at every stage is technologically significant, as it dictates steel quality as well as the service performance of various steel components. Inclusion free steels demand careful process conditions during various stages of refining treatment. Various steel plants are suffering from process interruptions such as ladle nozzle clogging, SEN clogging, break out etc during continuous casting of billets and blooms. It affects the day to day production in many folds. Problems related to castability mentioned above are mostly arises due to improper deoxidation and incomplete removal/modification of non-metallic inclusions in liquid steel. Steels produced for automotive and structural applications are aluminium killed, as it is a prerequisite for continuous casting of liquid steel. It is well known that, aluminium killed steels are seriously suffering from castability issues due to difficulty in removal of fine alumina inclusions formed in later stages of refining practice.

Ladle containing liquid steel is hold ideally for minimum of 10-15 minutes between argon rinsing/ladle refining station and before to start casting of liquid steel in continuous caster. During this period the liquid steel in ladle is subjected to only thermal convection and however, all possible natural convections are arrested. Slag metal interfacial reaction is expected to takes place during this period. Therefore, it is always expected that change in concentration of trace elements present in liquid steel. Elements like
aluminium, calcium, titanium, boron, magnesium etc are prone to diminish during these holding periods. A little change in these solutes causes significant changes in characteristics of non-metallic inclusion as well as hampers the thermo-mechanical processing of steels in later stages. Diminishing of aluminium (aluminium fade) in liquid steel indicates the formation aluminium oxide or aluminium nitride. Precipitation of alumina in liquid steel before casting ensures poor castability in continuous caster. It encourages nozzle clogging, SEN clogging, break outs and other quality defects in cast billets/blooms. However, owing to the high oxygen affinity, aluminium in liquid steel could not be avoided from fading. Detrimental effect of oxides precipitates in the later stages of refining on castability also should be controlled. The alumina particles formed during deoxidation by aluminium at the ARS or in later stages, if not controlled, also contaminate the final steel product and decrease the cleanliness index. These inclusions pose several metallurgical problems in the final steel. Ductility is appreciably decreased with increasing amounts of oxides and sulphides in steels [1]. Larger inclusions act as stress riser, which induce cracks in the finished products [2] and also they lower the resistance to hydrogen induced cracks [3]. Hard and brittle inclusions are also act cause for fatigue failure of steel components [4]. Therefore, in the present investigation efforts are taken to understand the effect of process parameters on aluminium fade in liquid steel during casting. Another aim of this investigation is to explore the scope to control the effect of aluminium fade such that, castability of aluminium killed steels should be maintained or improved. This paper provides a key understanding about the science behind the problem, and gives improved understanding to realize inclusion free steel.

2. The science of alumina formation and clogging
When the deoxidizer enters in to the liquid bath, it reacts with the dissolved oxygen in the melt to nucleate the oxidation product. Growth of particles follows the mechanisms includes Ostwald ripening [5], Brownian motion [6,7] and Stokes collision. Rising of oxide particles is naturally due to buoyancy, particles attachment to bubbles in gas stirred ladles and fluid transport also facilitates the oxide particles to float up to the top slag. It is also expected that some of the inclusions would stick to the refractory walls of the reactors.

The particles reaching the slag-metal interface have to react, separate and dissolve in the slag phase, which is governed by the dissolution kinetics of the particles in slag. It is further controlled by the composition, basicity, viscosity and melting temperature of the slag. Classical core reaction model [8] for dissolution manifests that up to 10μm, the rate limiting step is boundary layer diffusion and below 10μm, the rate limiting step is dissolution reaction between slag and inclusions.

Alumina inclusions are usually precipitates and grow in dendritic fashion, in high oxygen environment [9], cluster type in Al-killed steels [10] and coral like structure due to oswald ripening of dendritic clustered or clustered alumina inclusions [9]. Alumina inclusions readily form a three dimensional clusters (about 1 - 5μm) via collision and aggregation due to their high interfacial energy [11, 12]. However, small size particles are entrapped in the liquid steel as inclusions and therefore transferred to the downstream operations along with the steel matrix.

In the tundish, transport of deoxidation products to the nozzle wall is facilitated by fluid motion. Within the tundish recirculation zone, turbulent velocity fluctuations oriented in all directions. Fluctuations towards the tundish wall enable accumulation and deposition of inclusion [13]. Turbulent eddies present in the tundish, even in the absence of recirculation zone will transport deoxidation products to the nozzle wall [14]. Increased nozzle roughness also increases the probability of interception of entrained deoxidation particles present in liquid steel [13,15]. Due to various such factors that the agglomeration of solid inclusions takes place at the tundish nozzle and results in so called unwanted process interruptions during casing termed as clogging or choking of SEN. Not only alumina, but also calcium aluminates or calcium sulphides present in liquid steels have also been observed to be responsible for clogging in calcium treated heats [15,16]. Sintering of alumina particles takes place at temperatures above 1530°C [17], where the particle-wall or particle-particle bonding is relatively rapid [18] and assist for faster progress in clogging phenomena.

3. Plant data collection
A brief overview of the process route followed in an integrated steel mill from where the samples and
process data are collected for the present investigation is presented here. After tapping of liquid steel from the converter (BOF), the liquid steel is transferred to argon rinsing station (ARS) where chemical and thermal homogeneities are targeted. While rinsing with argon, aluminium wire is injected from the top to deoxidize the bath as well as alloying elements are added to meet the required chemical composition in predefined time period. If needed, the molten steel is taken to chemical reheating unit, to compensate the loss in temperature incurred during rinsing and transit between different. After all the secondary metallurgical operations are completed, the liquid steel is transferred to continuous casting section and teemed to the tundish for the commencement of casting.

Steel samples are collected from various sections (after tapping, ARS and during teeming) and it is analysed for the chemical composition using OES. Slag samples are also collected from the ARS, after completion of secondary metallurgical treatment. Slag samples are also analysed using XRF for the chemical composition.

### 4. Results & discussion

Based on the chemical analysis of steel samples collected from ARS and tundish, aluminium fade (difference in Al between ARS and tundish) is calculated and the results are presented in this section. Figure 1 shows the variation of various identified process parameters with aluminium fade for the studied heats.

Figure 1 (a) reveals that wt% aluminium fade proportionally increases with the amount of aluminium in liquid steel at tundish, irrespective of the steel grades. It could be attributed to the amount of aluminium present in liquid steel is more, causes the driving force available for aluminium fade high. Concentration gradient exist between liquid steel and top slag plays vital role in deciding the extent of fading in liquid steel refining process. Figure 1 (b) clearly shows the reverse trend for amount of aluminium added into liquid steel as deoxidizer. It is expected that the amount of Al added would be high for the heats/grades which have high wt% Al in steel composition. Eventually, Al present in liquid steel is high and also driving force for Al oxidation exists, even after ladle processing for various other reasons. Therefore, Al fade is expected to be high for the heats which consumes more amount of Al during secondary processing. However, the reverse trend observed for amount of aluminium added into liquid steel suggests that complete deoxidation. Such that alumina removal at early stage of process and also fine alumina inclusions find more time for floatation, otherwise alumina forms in latter stages as a consequence of aluminium fade. Therefore, these two contradicting factors originated for same reason and responsible for Al fade and decide the extent of alloying elements fading.

Figure 1 (c) shows that wt% aluminium fade increases steeply with increasing in tapping temperature of liquid steel in BOF convertor. Tapping temperature could be controlled by BOF convertor operational practice. It depends upon various process parameter such as after blow duration, end carbon, various additions during process like iron ore, lime, dolomite etc. However, importance of tapping temperature on Al fade needs to be addressed clearly. Very high tapping temperature would result in high amount of dissolved oxygen in liquid steel along with high amount of FeO in primary steelmaking slag. The residual FeO, which ever not reduced completely after deoxidation would be high for the heats tapped at high temperature from LD convertor. Therefore, improper slag killing always have adverse impact on recovery of alloying elements added during tapping and LRF station. Figure 1 (d) shows that Al fade increases gradually as the lifting temperature of liquid steel at LRF increases. In the standard industrial practice, liquid steel in ladle from BOF reaching at LRF station are having far lower than the temperature required by continuous casting section. Therefore, raising the liquid steel temperature to desired temperature at LRF station is one of the primary objectives. This effort of increasing liquid steel temperature at LRF causes substantial decrease in the aluminium present in liquid steel before casting due to driving force created by temperature increment.

Figure 1 (e) depicts the dependency of total rinsing time at LRF for liquid steel on aluminium fade. It shows that prolonged purging of liquid steel with argon either from bottom or top causes minimum aluminium fade before casting. This could be explained by the following reasons. Prolonged argon purging of liquid steel encourages excellent chemical and thermal homogeneity via., mixing. Once the system approaches the thermodynamic equilibrium, the slag - metal reaction is expected to complete. Therefore, the driving force for aluminium fade would not exist further and the fading occurs before
casting would be minimum. However, long term treatment of liquid steel at LRF will not always an encouraging industry practice. This would badly affect the availability of liquid steel for continuous casting section, since LRF is an intermediate section and expected to act as buffer between BOF and caster. Therefore, always an optimal time for LRF treatment should be identified and it should be maintained to avoid Al fade as well as to ensure continuous supply of liquid steel to caster.

![Graphs showing variation of aluminium fade with various process parameters](image1)

Figure 1: Variation of aluminium fade with various process parameters (a) wt% aluminium in steel, (b) weight of aluminium added as deoxidiser, (c) tapping temperature, (d) change in temperature of liquid steel between tapping and ARS and (e) total rinsing time at ARS

4.1. Reasons for formation of alumina

Though the reasons for aluminium fade exists in studied heats are discussed in previous section with various process parameters, a generic discussion on favorable conditions, prime reason for formation of alumina inclusion and the control measures in steel making practices are given in this section.

4.1.1. Deoxidation: Fe-Si, Fe-Mn are used as a deoxidizer in earlier days. Due to high residual silicon and manganese (≤ 0.5-1%) in the bath, now Aluminium is used as a deoxidizer in the form of wire/bar/shots. It results in dissolved oxygen content of below 5-20 ppm with residual Aluminium of 0.02-0.04%. This practice leaves alumina as a de-oxidation product and the respective chemical reaction as follows,
\[
2[\text{Al}] + 3[\text{O}] = (\text{Al}_2\text{O}_3)
\]

4.1.2. Desulphurization: Sulphur transfer from the metal to slag may take place with the help of CaO added into the liquid steel. The corresponding reaction could be presented as,

\[
\text{FeS}_{\text{steel}} + (\text{CaO}) = (\text{CaS}) + (\text{FeO})
\]

Oxygen liberated by this step also consumes aluminium or silicon. Hence, this process gives CaS as well as increased \(\text{Al}_2\text{O}_3\) content in the bath.

4.1.3. Refining Practice: Before the melt is taken to the continuous caster, the drop in temperature incurred during all the previous processing steps has to be compensated by heating the melt to the right temperature (super heat). However, in the plant, the Ladle Refining Furnace (LRF) is located away from the main processing line and also due electrical energy consumption and lengthy processing time in LRF, chemical heating is preferred by injecting aluminium wire along with oxygen blowing those results in exothermic reaction via., equation (1)

4.1.4. Basicity Decline: For efficient refining of steel, the slag basicity should be maintained in the range of 2.8 – 3.2. If the basicity of secondary slag lowers below 2.8, the slag becomes highly viscous and has low inclusion retention capacity. It also causes improper refining of liquid steel.

4.1.5. Slag eye area & Reoxidation: During argon rinsing practice, the injected argon gas bubbles rise through the melt, pushing the slag to sides leaving an opening in the top slag called as slag eye, which exposes metal to the atmospheric air and results in aerobic oxidation of alloying elements. With increase in gas injection rates the exposed area of liquid steel in the eye increases and results in increased oxygen pick up from the atmosphere. Apart from this, the transfer of liquid steel at any stage provide a chance for oxygen pick up, one such major instance being the exposed metal stream during the furnace tapping. All these re-oxidation costs excess aluminium which might end up as excess alumina inclusions. N.A.Mc Pherson et al [19] reported that, the nitrogen picks up between the tundish and mold is found to be 5 ppm. Considering 250 T heat and assuming all aspirated oxygen forms alumina, this would generate 1.4 Kg of alumina in two heats.

4.1.6. Slag Carry Over: During steel making, the liquid steel passes through a number of metallurgical vessels. While transferring from one vessel to other, there should be some slag drained inadvertently along with the metal known as slag carry over. This is deleterious, especially the BOF slag, because of its oxidizing nature, the carried over slag interacts with the lining (fireclay consist of \(\text{SiO}_2\) and \(\text{Al}_2\text{O}_3\)) and lowers basicity which favors phosphorous reversal from slag to metal phase. Apart from the problem of phosphorous reversion, this also necessitates increased addition of Al which results in increased alumina formation.

4.1.7. Inclusion Size: Stokes rise velocity for large size particle is higher than the smaller size particle. Therefore, that the smaller particles remain entrapped in the liquid steel. Argon rinsing assist agglomeration and coagulation of inclusion, so that inclusions can float up to the slag phase. However, it is experienced that floatation of fine alumina inclusions are challenging task for the steelmakers to produce extra clean steels.

4.2. Challenging Remedies:

4.2.1. Calcium Treatment: Calcium addition (Ca-Si powders filled in steel tubes) transforms pure \(\text{Al}_2\text{O}_3\) to calcium aluminate inclusions, which is expected to possess liquid state at 1873 K, when the CaO content has reached 35%. If the Ca amount is too small, solid aluminites are formed \(\text{CaO}.6\text{Al}_2\text{O}_3\), \(\text{CaO}.2\text{Al}_2\text{O}_3\), \(\text{CaO}.\text{Al}_2\text{O}_3\)), which are even more detrimental than alumina inclusions with regard to nozzle clogging [14, 20].
It forms calcium aluminate

\[ 3 \text{[Ca]} + \text{<Al}_2\text{O}_3\text{>inc} = 2 \text{[Al]} + 3 \text{(CaO)} \]  
(3)

\[ 3 \text{<CaO>inc} + 2 \text{[Al]} + 3 \text{[S]} = 3 \text{<CaS>inc} + \text{<Al}_2\text{O}_3\text{>inc} \]  
(4)

In high sulphur steels (S>0.005%) the injected calcium causes desulphurization rather than inclusion modification, as explained by the above mentioned chemical reactions. It forms calcium aluminate inclusions surrounded by CaS rich rim of small size (5μm) that are easily deformable and therefore, mechanical properties of the steel would not adversely have affected. Calcium treatment cannot be suggestable recommendation for the steel plants operating with high sulphur content in liquid steels (> 100ppm).

4.2.2. Slag arresting using DART: DART is a device made of refractory used to control the slag carry over in BOF converter during tapping. The material of the DART should have density value in between steel and slag, such that it floats near to the interface and prevents carry over during tapping process. Improper calibration and positioning of DART are the problems associated and it is not a reliable device to control slag carry over in day to day practice for quality steel production.

4.2.3. Ar Injection through Stopper Rod: It is also a proposed mechanism being practiced in steel plants for instant removal of alumina deposited (clogging) in the tundish outlet i.e, mouth of the SEN. The cylindrical arm with argon injection facility is inserted right upright above the tundish outlet causes flushing of the deposits. The solid particles present in the choked region will enter into the solidifying strand and remain in the product as an inclusion. Therefore, the choking problem cannot be solved without compromising the steel quality.

4.3. Control Measures:
- Sulphur control right from the blast furnace avoids reaction (2 and 4) during steel refining practices. Employment of external de-sulphurization unit as a hot metal pre-treatment, addition of lime during tapping from BOF irrespective of the grade will decrease the sulphur content in liquid steels. The latter process improves cleanliness of steel, thereby decreasing the aluminium consumption and maintaining the appropriate basicity of secondary slag.
- Once, the sulphur content of the hot metal is controlled by either way, calcium treatment helps to modify the inclusion.
- Synthetic slag formation/addition helps to trap the inclusions present in liquid steel. The favourable slag of that kind is CaO- 50 % SiO2- 7 % Al2O3:43 and should have a melting temperature lower than 1350°C [22].
- Installation of IR-Camera with slide gate mechanism to control the slag carry over during liquid steel transfer practice from one metallurgical vessel to other vessel.
- Employing ladle furnace in the on-line mode, thereby temperature drop can be adjusted by electrical heat rather than the chemical heating practices.
- Optimization of argon rinsing practice is required to control the slag eye opening and hence oxygen picks up and alloying elements fading can be minimized.
- In ARS, the heat should be finished with a gentle rinsing, which will let the smaller alumina to agglomerate and float up with much less temperature drop and re-oxidation.

These types of process modifications will assist to some extent to improve the alumina formation, thereafter reduces nozzle clogging. Apart from these, the present investigating authors suggest to re-engineering of the tundish design for enhanced floatation of inclusion.

- Re-Engineering of Tundish Design: Tundish being a reservoir for molten metal in continuous casting operation plays a major role in removal of inclusions to float out. This is facilitated by efficiently modifying the flow fields by using flow modifiers. For instance, L.Zhang et al [23] studied the inclusion removal efficiency and reported that the flow control devices are favorable
for the inclusion removal. The total removal ratio is 51 wt% without flow control devices and the inclusions bigger than 72μm in radii can be totally removed. The total removal ratio is 79 wt% with flow control devices and the inclusions bigger than collision 61μm in radii can be totally removed. After a decade, Rajasekar [24] improved the tundish design with flow modifiers, his mathematical model based on population balance approach suggests that, operating the tundish at higher bath height and higher flow rate one can attain the inclusion removal efficiency of about 82.85% and the number density of inclusion larger than 35μm is significantly less in value. Zhang et al [25] summarizes from various research works towards inclusion control that, the two-layer (upper layer- rice hull; lower layer – low melting basic flux) flux practice in tundish, protection by argon gas from steel shrouding from ladle to mold, new techniques at SEN (such as swirl nozzle technique, step nozzle technique, multiport nozzle, and oval offset bore throttle plate etc.) are quite useful and promising techniques. Hence, the authors suggest to re-engineer the tundish design along with process modifications, such that the choking problem may be solved without contaminating the final product and hence the dream of clean steel could be realized.

5. Conclusions
Investigation carried out provided a chance to study the alumina formation at successive stages in steel making operations. This paper emphasizes the science of-alumina formation, influence of plant practice in aluminium fade and hence, formation of alumina. At the end it suggested some process modifications to reduce the population of alumina and also it is recommended to re-engineer the tundish design for tackling the choking problem towards clean steel production.

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