Calcium Wire Ladle Treatment to Improve Cleanliness of Centrifugally Cast Steel

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ABSTRACT

Centrifugal casting provides the unique opportunity of combining improved melt refining techniques with large centrifugal forces and directional solidification during casting to reduce the non-metallic inclusions in the final product. In this paper, the effects of calcium wire injection on the number, size, composition and morphology of non-metallic inclusions in centrifugally cast products are evaluated. Calcium-bearing wire was fed into the liquid steel in the ladle prior to centrifugal casting. Samples were collected throughout the steelmaking and casting processes starting at argon oxygen decarburization (AOD) and continuing through the centrifugally cast product. Samples were analyzed on the Aspex PICA 1020 for quantitative inclusion analysis. The effects of calcium treatment combined with centrifugal casting on inclusions and mechanical properties are discussed.

Keywords: Calcium-bearing wire, centrifugally cast steel, automated inclusion analysis

INTRODUCTION

Low alloy cast steels suitable for high pressure service are often manufactured using centrifugal casting. To meet the mechanical specifications for pressure vessels, low alloy cast steels undergo extensive processing steps to improve steel cleanliness. One primary defect reducing the quality of steel castings is non-metallic inclusions produced during the steelmaking and solidification processes. Non-metallic inclusions degrade the quality or “cleanliness” of the cast steel with increasing volume fraction, diameter, or size, and with uneven or localized distribution, as well as amorphous morphology. Therefore, the manufacturing process of low alloy steel must be carefully controlled to improve the mechanical properties.

The “cleanliness” of cast steel products can be improved through inclusion flotation. After aluminum deoxidation, the aluminum oxide rich inclusions start floating to the surface where they are incorporated into the ladle slag. However, in industrial practice, the time interval between aluminum deoxidation of the liquid steel in the ladle and pouring the mold is not sufficient for inclusion flotation, especially for small (<2 µm) non-metallic inclusions. Most of the alumina inclusions are small and remain in the molten steel. The purpose of calcium treatment after aluminum deoxidation is to modify the composition of alumina inclusions and form low melting point calcium aluminates that float at a faster rate and produce cleaner liquid steel. Low melting aluminates, consisting of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$, and $\text{CaO} \cdot \text{Al}_2\text{O}_3$, melt in the temperature range of 1395-1605°C (2543-2921°F) (Figure 1). The melting temperature for calcium aluminates is significantly lower than the alumina inclusions (2072°C[3762°F]).

Low melting point non-metallic inclusions are easier to remove from the molten steel because they have a strong possibility of recoalescence. In addition, Ca inclusion modification reduces the tendency for the modified inclusions to attach to the refractory surface preventing nozzle blockage during teeming and continuous casting. In addition, manganese and calcium sulfides ((Mn, Ca) S) can be formed as bi-phase inclusions during calcium treatment. A bi-phase inclusion is composed of an oxide prime phase surrounded by a sulfide secondary phase. Typically, (Mn, Ca) S forms around the $\text{CaO} \cdot \text{Al}_2\text{O}_3$. The oxisulfide inclusions form round Type I inclusions, providing better mechanical properties when compared to other types of inclusions.

![Fig. 1. CaO-Al₂O₃ phase diagram.](image)

EXPERIMENTAL

Medium carbon, low alloy cast steel (0.21 %C, 0.21 %Si, 0.63 %Mn, 2.6 %Cr, 0.12 %Ni, 0.79 %Mo, 0.012 %P, and 0.001 %S) was melted in an EAF followed by AOD. After the final additions in the AOD, the molten steel was centrifugally cast into large diameter tubes (~17" Outside Diameter, ~12" Inside Diameter, 22' long). Three heats were tested and analyzed. These heats included the Base Heat A with no calcium addition, and calcium treated Heats B and C. Heats B and C were calcium treated using a steel clad pure calcium wire in the ladle prior to centrifugal casting. Table 1 shows the composition of the 9 mm diameter calcium wire used during the experimental calcium treated heats. The calcium wire was injected using a PC-Micro wire feeder with approximate 17 ft/min injection speed.

The aim Ca additions were based on treating steel containing 0.06 wt. % dissolved aluminum [Al]_{ds} in the ladle to produce low melting CaO•Al₂O₃ and 12CaO•7Al₂O₃ phases. The treatment was done to decrease inclusions through additional floatation and modify the shape of the remaining inclusions to enhance the mechanical properties. Table 2 shows the ladle capacity for each heat and the aim % calcium added in the ladle prior to centrifugal casting. Heat B was fed with relative low calcium content (0.014 % Ca) due to the rapid thermal losses in the ladle during the calcium treatment.

Lollipops samples were collected directly from the molten steel using a submerged sampler for inclusion analysis. Centrifugally as-cast samples from the end of the finished tube were also collected for inclusion analysis and impact testing. A schematic representation of the as-cast tube samples showing the location from the inside to the outside of the cast product is given in Figure 2. The inclusion analysis results of each as-cast tube were divided into three regions. The three regions represent a part of a whole (1/4 or 0.25, ½ or 0.50, ¾ or 0.75). The final product region was the average of three samples at x=0.25, x=0.50 and x=0.75. The inside diameter (ID) at x=0 and the outside diameter (OD) at x=1 are typically removed through machining and not incorporated in the final product.

Fig. 2. Schematic representation of the as-cast tube sample taken from the end of the finished tube showing the location from the inside to the outside of the cast product.

The specimens were polished to 1,200 grit and final polished with 0.1 µm diamond paste using the Abramin auto-polishing machine. An approximate area of 9.8 mm² was used for the inclusion analysis on each lollipop and as-cast tube specimen using the Aspex PICA 1020. Duplication of results was performed by taking the average value of three tests performed in the same location of the specimen.

Centrifugally as-cast tube samples from each heat were heat treated before mechanical testing. The heat treatment was based on the standard specification for steel castings suitable for pressure service (ASTM A-487). The centrifugally cast samples were austenitized at 954°C (1750°F), water quenched followed by tempering at 613°C (1135°F) and furnace cooling to below 316°C (600°F). Charpy impact tests were performed on Heat A (base case), Heat B (0.014% Ca) and Heat C (0.077% Ca) using three samples for each test.

RESULTS

The number of inclusions/mm² and percent area covered by inclusions for the ladle specimens and final product (average of the three samples at x=0.25, x=0.50 and x=0.75) of each as-cast tube sample are displayed in Figures 3 and 4. Note that there are only limited samples for some of the locations. Missing samples does not indicate an absence of inclusions.

The number of oxides/mm² for all heats, especially the aluminum containing oxides, regardless of calcium addition decreased from the AOD to the final product (Figure 3). Heat B (0.014% Ca) was the case where it was possible to perform inclusion analysis at all stages of the ladle treatment and casting process. This heat demonstrated that the small calcium addition did not change significantly the population of the oxide inclusions. The Ca-treatment for Heat B had a minor effect on the inclusion composition in the ladle. However, it does demonstrate the decrease in the number of
inclusions from AOD through ladle treatment to the final product as a result of natural inclusion flotation. In both Heat B (0.014% Ca), and Heat A (Base Case), an increase in the number of Mn rich inclusions was observed in the final product, an indication of reoxidation.

The number and volume of alumina inclusions/mm² decreased dramatically from the ladle to the final product for both Heats A (Base Case) and C (0.077% Ca). Heat C was treated with the highest Ca addition (0.077% Ca) and exhibited different trends in comparison to the no Ca treated heat A. Despite the fact of a larger amount of inclusions after the final additions in AOD for Heat C, the Ca-treatment modified the inclusion composition. Simultaneously, the Ca-treatment decreased the number of inclusions/mm² and the total inclusion volume in the final casting in comparison to the ladle after the final additions in AOD and before treatment (Figures 3 and 4). The alumina inclusion population decreased in the final casting by more than five times.

The large amount of inclusions, especially at the OD, might be due the fact that the refractory surface tends to oxidize at the beginning of the casting. The superficial oxidation produces carbon monoxide between the refractory and molten steel interface (Cs + 1/2 O₂ = CO). The carbon monoxide from the refractory and other emitted gasses from the molten steel and environment reoxidize pre-existing particles that form new inclusions.

On the other hand, the number of inclusions/mm² for heat C, especially Al₂O₃ and Mn-Al-O inclusions, decreased dramatically in the final product of the calcium treated Heat C (0.077 % Ca). In addition, most of the Al₂O₃ inclusions were transformed into calcium aluminate inclusions.

Outside diameter (x=1) (Figures 5 and 6). Theoretically, the inside diameter of the centrifugally as-cast tube should contain a larger amount of low-density inclusions than the rest of the cast product because of the centrifugal forces. However, it was observed in Figure 5 that the highest amount of inclusions/mm² was concentrated in both the outside diameter (OD) and inside diameter (ID).

Inclusion analysis was performed on the as-cast tube samples which were split into regions representing the final product (average of the three samples x=0.25, x=0.50 and x=0.75), the inside diameter (x=0) and the outside diameter (x=1) (Figures 5 and 6). Theoretically, the inside diameter of the centrifugally as-cast tube should contain a larger amount of low-density inclusions than the rest of the cast product because of the centrifugal forces. However, it was observed in Figure 5 that the highest amount of inclusions/mm² was concentrated in both the outside diameter (OD) and inside diameter (ID).
Centrifugally cast tube samples were heat treated prior to Charpy impact testing. Heat treatment included austenitization at 954°C (1750°F), water quenching followed by tempering at 613°C (1135°F), and furnace cooling to below 316°C (600°F). Average Charpy impact results (Table 3) show that the impact energies for Heats B (0.014% Ca) and Heat C (0.077% Ca) were larger than the base Heat A. This means that some degree of transformation and reduction of non-metallic inclusions by Ca-treatment positively influenced the impact energy.

Table 3. Average Charpy Impact Energy (ft*lb) of Steel in the Three Calcium Injection Experiments.

<table>
<thead>
<tr>
<th>Heat</th>
<th>Heat B (0.014% Ca)</th>
<th>Heat C (0.077% Ca)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat A (Base Case)</td>
<td>83.1 (SD ± 1.01)</td>
<td>89.7 (SD ± 3.57)</td>
</tr>
<tr>
<td>Heat B (0.014% Ca)</td>
<td></td>
<td>84.9 (SD ± 1.05)</td>
</tr>
</tbody>
</table>

Figure 7 is a quality assessment of the centrifugally cast products after heat treatment and Charpy impact testing. The combination of higher hardness (strength) and higher impact values for Heats B and C indicates a better overall quality combination than the untreated Heat A. This indicates that Ca-treatment provided better mechanical properties through the modification and transformation of detrimental non-metallic inclusions.

**MODELING**

During solidification, centrifugal castings experience forces that are orders of magnitude larger than the force of gravity that is experienced in static sand molds. This difference can be presented by the $G_{\text{factor}}$ which is calculated using the peripheral velocity ($V$, m/sec), casting radius ($r$, m), and gravity acceleration ($g$, m/s²):

$$G_{\text{factor}} = \frac{V^2}{rg}$$

Equation 1

The $G_{\text{factor}}$ could vary from 50 to 200 for large centrifugally cast tubes having a tremendous effect on non-metallic inclusion flotation. Figure 8 shows the solidification kinetics using a tube wall thickness of 100 mm (4”) and an internal layer of packed sand. The packed sand was 25.4 mm (1”) thick and the steel flask was 25.4 mm (1”) thick. The dashed line represents the position of the liquidus whereas the solid line exhibits the solidus. The solidification kinetics is plotted versus the cooling time of the molten steel poured at 50°C superheat. Most of the casting volume solidified unidirectional from the OD with development of a wide mushy zone. The rest of the casting volume, which is composed of a very thin layer, solidified from the inside diameter (ID) during the final stage of the casting process. These conditions can be varied depending on the intensity of the heat transfer at the ID. For example, a thin layer of slag forming on the ID can provide sufficient insulation to allow full unidirectional solidification.
Fig. 8. Solidification kinetics in a centrifugally cast tube using a wall thickness of 100 mm (4”).

The cooling time from Figure 8 was used for flotation analysis on non-metallic inclusions during the casting process. Fluent Software was used to model two-dimensional inclusion flotation. A stagnant melt was chosen after pouring into a steel flask mold using the “Discrete phase model”. Figure 9 shows flotation dynamics assuming spherical non-metallic inclusions through a wall thickness of 100 mm (4”). The stagnant melt was cooled in a sand mold (1G) and in centrifugal mold (100G). The period for superheat removal, in which the melt is above the liquidus, is also shown by the shaded area in Figure 9. At this period of time, the non-metallic inclusions smaller than 10 µm diameter were not removed from the sand casting. In contrast, centrifugal forces accelerated inclusion flotation and particles with a diameter larger than 2 µm were removed completely from the melt in a short period of time. These particles were removed before the melt could cool from the pouring temperature to the liquidus temperature. In reality, some melt motion is produced in the sand mold due to thermal convection. In centrifugal casting, the melt can be displaced through mold vibration. In both cases, the particle movement forces are less when compared to the simulated centrifugal forces at 100G.

Fig. 9. Fraction of non-metallic inclusions removed by flotation with diameters from 2 µm to 10 µm in sand mold (1G) and centrifugal casting (100G).

If the centrifugal forces have the possibility of non-metallic inclusion removal from the molten steel when above the liquidus in a short period of time, only the inclusions growing in the liquidus-solidus mushy zone (endogenous inclusions) would be trapped in the casting. The main hydrodynamic reason for flotation deceleration of non-metallic inclusions is the rapid increase of viscosity in the mushy zone. When the liquid phase contains some amounts of solid phase, the effective ($\eta_r$) of the system will increase. The effective or apparent viscosity ($\eta_a$) of a heterogeneous system depends significantly on the fraction of a solid phase ($f$), as well as the liquid phase viscosity ($\eta$). These parameters can be calculated using the Einstein’s ($\eta^e$) (solid line), Jeffery’s ($\eta^e$) (dashed line) equations or the equation used by Pretorius ($\eta^e$) (dotted line) in Figure 10.

Fig. 10. Effect of solid phases on the apparent dynamic viscosity ($\eta_a$) of molten steel.

The estimated effect of the apparent liquid phase viscosity ($\eta$) on inclusion flotation in the mushy zone in the centrifugally cast tube at 100G is given in Figure 11. The simulated wall thickness was 100 mm (4”) and the diameter of the non-metallic inclusions was 5 µm. The data shows that even under the influence of large centrifugal forces, the flotation of inclusions is dramatically decreased in the mushy zone due to the apparent liquid phase viscosity ($\eta_a$) increase. This indicates that a significant number of small non-metallic inclusions would not float to the tube ID but be trapped in the casting due to the solidified melt with a large apparent liquid phase viscosity ($\eta$).

Fig. 11. Effect of the apparent liquid phase viscosity ($\eta_a = 0.005$ kg/ms without solid fraction, $\eta_{ap} = 0.05$ kg/ms with 25-30% solid fraction) on flotation dynamics using non-metallic inclusions of 5 µm in diameter.
Calculation of the non-steady state solidification with different apparent liquid phase viscosities (\(\eta\)) in the mushy zone of the centrifugal cast product was performed in Figure 12. Non-metallic inclusions 5 µm in diameter formed at different temperatures were evaluated. The non-metallic inclusions located in the casting region at a temperature above the liquidus had sufficient time to be released while a significant amount of non-metallic inclusions located in the mushy zone were trapped in the centrifugally cast tube.

**DISCUSSION**

Based on the experimental results, modeled solidification kinetics and flotation dynamics, all types of non-metallic inclusions in the centrifugal casting process could be classified into two main groups:

- Group 1 comprises exogenous non-metallic inclusions, from different outside melt sources including large particles from the slag, refractory and product reactions with mold materials. This group of inclusions may not affect the mechanical properties of the centrifugally cast tube because they will be forced to the ID or OD due to the centrifugal forces in the casting process. The ID and OD of the centrifugally cast tube are usually removed by secondary machining.

- Group 2 includes endogenous non-metallic inclusions growing directly in the molten steel, which could be subdivided into three subgroups:
  
  a) Prime non-metallic inclusions, formed in the molten steel as a result of de-oxidation, de-sulfurization and other reactions with active components in the melt (e.g. nitrides). The prime non-metallic inclusions are smaller than the exogenous group. The prime nonmetallic inclusions are forced to the ID and OD due to the centrifugal forces in the casting process.

  b) Re-oxidation products, formed when the molten steel is exposed to air during mold filling. Typically, these inclusions are small and can be removed from the melt before formation of the mushy zone, while some part of these inclusions could be trapped near the OD surface of centrifugally cast tube.

  c) Secondary non-metallic inclusions, formed near the liquidus temperature and inside the mushy zone. Two main mechanisms can promote the formation of secondary inclusions. The first one is due to the thermodynamic affinity of free radicals in the molten steel that interact with the remained impurities (sulfur and oxygen). The second mechanism includes inclusion segregation of free radicals in the remaining portion of the molten steel during dendrite solidification. Figure 13 shows the inclusion segregation mechanism for MnS using the Scheil model. It was observed that more stable inclusions (\(\text{Al}_2\text{O}_3\), \(\text{Al-Ca-O}\) and \(\text{CaS}\)) were mainly formed above the liquidus temperature and their concentrations did not significantly changed during solidification. Sulfur segregation and increasing activity of \(\text{Mn}\) and \(\text{Si}\) radically promoted \(\text{MnS}\), \(\text{Mn-Si-O}\) and \(\text{Mn-Si-Al-O}\) complex inclusion in the mushy zone during solidification. This subgroup of inclusions could be trapped by the mushy zone located in the centrifugally cast tube.

Fig. 13. Thermodynamic prediction (Scheil model) of complex inclusion formation (\(\text{MnS}\), \(\text{Mn-Si-O}\) and \(\text{Mn-Si-Al-O}\)) in the mushy zone during solidification (FACTSAGE software).
The sand casting products may be composed of a combination of exogenous and endogenous non-metallic inclusions in the final product. Figure 14 shows that the centrifugal forces could drive most of the exogenous, prime and re-oxidation non-metallic inclusions to the ID and OD of centrifugally cast tube. This reduces significantly the amount of these detrimental inclusions in the final product of the centrifugal cast tube, especially when the molten steel is calcium treated prior to casting. Therefore, the only type of inclusions formed in the final product of the centrifugally cast tube is the secondary non-metallic inclusions.

**Fig. 14. Comparison of the evolution of non-metallic inclusions during sand mold gravity casting process and AOD-Ca treated centrifugal casting process.**

CONCLUSIONS

Inclusion analysis and impact testing was performed on centrifugally cast large diameter tubes. The effects of the Ca-wire ladle treatment prior to casting using 0.014% and 0.077% Ca were compared to the base heat with no calcium treatment. It was observed that the Ca treatment modified to some extent the types of inclusions and influenced the inclusion population at different locations of the centrifugally cast tube. In particular:

- The \( \text{Al}_2\text{O}_3 \) and \( \text{Mn-Al-O} \) inclusions were reduced and transformed into low melting calcium aluminate inclusions in the final product of Heat C (0.077% Ca) whereas there was minor inclusion modification in Heat B with a low calcium ladle addition (0.014% Ca). The majority of the percentage area covered by inclusions in the final product of Heat C (0.077% Ca) corresponded to modified Ca-Al-O inclusions.

- Both Ca-treated heats showed increased toughness while the impact energy for Heat B (0.014% Ca) was larger than heat C (0.077% Ca) due to independent effect of refining practices in AOD.

- The \( \text{Al}_2\text{O}_3 \) and \( \text{Mn-Al-O} \) inclusions were increased in terms of number and near the OD and ID locations for calcium treated heats. This indicates that the exogenous, prime and re-oxidation non-metallic inclusions were forced through intensive flotation from the melt to the ID and OD, leaving behind the secondary non-metallic inclusions in the mushy zone of the cast tube. These processes were also simulated.

- Large calcium additions in the molten steel prior to casting (based on the aluminum containing oxides), less injection time, better mold refractory, less fluid turbulence in the pouring basin, among other factors will increase the potential for success in transforming alumina inclusions into lower melting calcium aluminates (\( \text{CaO} \cdot \text{Al}_2\text{O}_3 \) and \( 12\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \)) to enhance the impact properties of the centrifugally cast tube.

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