A Possible Reason Why Ti-SULC Grades Are More Prone to CC Clogging Issues Than Other Al-Killed Grades


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(*) now retired

ABSTRACT

TiSULC grades are known to cause more casting problems than other Al-killed grades. The occurrence in these grades of oxide inclusions exhibiting specific shape (“veils”), consisting mainly of alumina with various contents of Ti oxides is often believed to the source of these problems. Some studies have shown that these inclusions could be formed during Ti addition due to temporarily local high concentrations in this element. In this study, it is the effect of accidental reoxidations in tundish which has been investigated. These reoxidations are modeled with the same equations as for selective oxidation i.e. by combining local thermodynamic equilibrium and diffusion Fick's equations. When comparing the model outputs for TISULC and Al-killed grades, it appears that, in both cases, reoxidations result ultimately in spherical alumina build-ups formed at some distance of the reoxidation “sources”, but these build-ups are much denser in the case of the TISULC grades and consequently more prone to a sintering phenomenon and therefore less easily dispersed by the liquid steel flow. These build-ups are believed to be at the origin of some of the veils observed in TISULC grades.

Keywords: Clogging; TISULC; reoxidation; thermodynamics; diffusion

INTRODUCTION

Inclusions presenting long filaments and forming veil-shaped clusters are often observed in TISULC grades (Figure 1). SEM analyses show that they consist mainly in Al-rich oxides, sometimes containing Ti oxides and Ti nitrides. The castability difficulties encountered for these grades are often attributed to these veils: their large dimensions make them prone to stick to the continuous casting refractory pieces and then to disrupt the liquid steel flow.

Figure 1. Veil cluster in a TISULC grade (†).

The presence of Ti oxides detected in some clusters is often thought to be at the origin of this specific morphology but the mechanism remains unexplained: if reoxidation, when strong enough, affects Ti and yields, at least in a transient state, to mixed Al-Ti mixed oxides, no satisfactory explanation exists which links Ti local oxidation and/or subsequent Ti-oxide reduction to this morphology.

The objective of this memo is to propose a possible mechanism based on a model combining diffusion in liquid steel and oxide precipitation. This model can explain the difference of castability between these TISULC grades and Al-killed grades.
THE MODEL

Figure 2 shows a recent SEM automatic inclusion analysis (ASCAT) performed on a lollipop sample from tundish of TiSULC grade with a high oxygen level (43 ppm). It was analyzed with MaLIA software (Machine Learning for Inclusion Analysis developed by ArcelorMittal Global R&D). It shows a complex inclusion structure formed by several concentric sub-structures. The smaller structures (red rectangle of the figure) clearly present a progressive change of composition: their centers are mainly made of FeO/MnO oxides, surrounding by zones progressively getting richer in Ti and then in Al oxides. This is believed to be the very first steps of the reoxidation phenomenon which finally gives birth to the inclusion veils.

![Figure 2: Veils of inclusions (blue dots) and FeO-MnO macro inclusions detected by ASCAT on the left, analyzed by MaLIA software on the right with classification of inclusions.]

This observation evokes the selective oxidation phenomenon which occurs during the annealing process. During this process, the surface chemistry of steel sheets is affected by the interaction between the oxygen of the atmosphere and the steel surface: traces of oxygen, present in the annealing atmosphere, diffuse inwards, the oxidizable elements diffuse outwards and consequently various oxide precipitates are formed in the sub-surface alloy region (Figure 3). One main difference between the selective oxidation and reoxidation, apart from, of course, the different temperatures involved, is the fact that, in the latter case, the oxygen source vanishes with time whereas it is constant for the selective oxidation phenomenon.

![Figure 3: Selective oxidation phenomenon.]

Therefore, the computer code built to model this phenomenon is based on the same architecture as the so-called DIFFANI model of selective oxidation (2). It couples the diffusion equation (Fick's equation) in spherical coordinates and thermodynamic equilibrium precipitation. For the sake of simplicity and because of a lack of experimental data, local equilibrium is supposed to be reached instantaneously (no nucleation step in particular). Therefore, the only kinetic limit is due to the transfer of the elements in the steel. The thermodynamic description is brought by CEQCSI which calculates at each time step and for each “cell” the nature, amount and composition of the oxides. In particular, CEQCSI uses the GCA slag model (3) to simulate the precipitation of complex liquid oxides containing Fe, Al, Si, Mn and Ti oxides together with other...
solid stoichiometric or multicomponent oxides. Figure 4 shows the Fe-Al-Ti phase diagram for a grade containing 0.3wt%Mn and 0.05wt%Si obtained at 1540°C with this model. A large domain of liquid oxides exists in the center of the diagram and is reached by reoxidation inclusions in Al killed steel grades. The range of composition of these liquid oxides is very large: they contain mainly Al and Ti oxides for weak reoxidation conditions (low oxygen activities – upper part of the diagram) and get more and more enriched in oxides of less oxidable elements Si, Mn and Fe in strong reoxidation conditions (high oxygen activities – bottom left part of the diagram).

![Fe-Al-Ti phase diagram at 1540°C (0.3wt% Mn – 0.05wt%Si) calculated with CEQCSI. Light lines correspond to iso-values of oxygen activity.](image)

In the model, the reoxidation source is a spherical “droplet” of iron oxides placed in the center of the modeling domain. The amount of the oxide – the radius of the droplet – will determine the “intensity” of the reaction. The origin of this oxide could be, for instance, a violent interaction of the steel with the atmosphere at the surface of the reactor, this oxide is then entrained away from the surface by the liquid steel flow. This comes to consider this reoxidation phenomenon as a 2-step process: (i) “oxygen intake” = a violent and sudden capture of oxygen by the metal which is locally completely transformed into Fe-oxides followed by (ii) “oxygen release” = a “return” to an equilibrium – or, as will be shown, to a steady state – by diffusion of the oxygen into the bulk of the metal. The objective of the present model is to describe only this second step.

The main physical parameters controlling the phenomenon are thermodynamic (i.e. the solubility products and the mixing models) and kinetic. The thermodynamic parameters are the ones selected or, for the mixing parameters of the GCA slag model, carefully assessed in CEQCSI (which are used for calculating the phase diagram here above). The kinetic parameters are the diffusion coefficients of the steel solutes. Their values at 1540°C (temperature chosen for the examples presented in this report) are listed in Table 1.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Diffusion Coefficients (µm².s⁻¹) at 1540°C in Liquid Steel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>3020</td>
</tr>
<tr>
<td>Mn</td>
<td>4210</td>
</tr>
<tr>
<td>Si</td>
<td>1320</td>
</tr>
<tr>
<td>Ti</td>
<td>7510</td>
</tr>
<tr>
<td>N</td>
<td>9190</td>
</tr>
<tr>
<td>O</td>
<td>9750</td>
</tr>
</tbody>
</table>

**A SIMPLE SYSTEM: FE-AL-O**

To illustrate the phenomenon modeled in this report, a first simple case has been considered corresponding to a reoxidation of a pure Fe-0.03wt%Al alloy at 1540°C. A spherical domain of 80 µm has been taken into account containing initially 20 ppm of total O. The reoxidation caused by the FeO droplet put in the center of the domain at the initial stage corresponds to an additional oxygen content of 70 ppm for the domain considered for the calculation.

Figure 5 gives the composition of the inclusions at different times. The source of the reoxidation clearly appears at the left-hand side. As mentioned before, it is composed of pure Fe oxides occupying initially a sphere of 2.5 µm. The rest of the domain is populated with deoxidation inclusions i.e. alumina. Already, at 0.01s, a zone of mixed oxides (Al₂O₃-FeOₓ) appears in
between the zones of pure Fe oxides and of pure alumina. Then, very rapidly, all Fe oxides are reduced and, at 1 s, the whole domain is occupied by alumina.

Figure 5. The inclusions composition and amounts in the different cells at 0.01, 0.05 and 1s (system Fe-Al-O).

Figure 6 gives the dissolved oxygen and dissolved aluminum gradients at the same time steps as in Figure 5. It also gives the distribution of the alumina inclusions throughout the domain. An alumina build-up is formed in the region of the intersection of the 2 gradients. With time, the shape of the alumina build-up changes and the position of its maximum value moves away from the reoxidation source. At 1s, dissolved oxygen and aluminum gradients are flat, meaning that, without steel movement, the distribution of the inclusions will not change anymore.

Figure 6. Oxygen and aluminum content gradients and amount of alumina at 3 different times. Al and O contents given on the graphs are expressed in ppm per ton of steel.

This example illustrates the consequences of a reoxidation event: the formation of a very stable alumina build-up (or cluster) of spherical shape at a certain distance from the source of the reoxidation itself. The shape, density and distance from the reoxidation source of the alumina cluster depends on the Al and on the oxygen quantity brought by the reoxidation. As a consequence, quantifying a reoxidation event in terms of additional ppm's of O per ton of steel brought to the metal has little meaning since it comes to averaging, over the whole mass of metal, the surplus of alumina which is, on the contrary, not at all distributed homogeneously.

REOXIDATION OF A TISULC GRADE

The case considered in this paragraph is a TISULC grade containing 0.03wt% Al, 0.3wt%Mn, 0.05wt%Si, 0.06wt%Ti, 90 ppm N and initially 20 ppm O. As in the example presented here before, reoxidation is simulated by a pure FeO droplet of 2.5 µm placed in the center of the modeling spherical domain. Figure 7 captures the very first moments of the process. We observed after 0.01 s (central diagram) starting from the center:
- The reoxidation source formed by pure Fe oxides.
- A zone of mixed oxides, successively enriched in MnO, to a limited extent in SiO₂ and TiOₓ, the external zone of this region being mainly a mixture of Al and Ti oxides. This evolution of composition is guided both by the oxidability of the different elements (“Fe<Mn<Si<Ti<Al”) and by their abundance in the grade.
- Further away from the reoxidation source, a zone containing a noticeable amount of TiN. The local content of nitrides is given by the right-hand side diagram. This precipitation of TiN is due to the oxidation of the metal which,
consequently, gets enriched in N which diffuses in the rest of the metal. It must be emphasized that, in this calculation, no additional N amount has been supposed to be brought to the metal by reoxidation.

Figure 7. Very first moments of a TISULC grade modification.

Figure 8 describes the evolution in the next moments. The TiN zone shrinks and disappears very quickly, Ti being oxidized by the diffusing oxygen. The domain occupied by the mixed oxides expands first and, in the same time, the reduction of the reoxidation source begins: the Ti oxide content of the outer zone increases, the MnO content of inner zone increases as well. These results corroborate quite well with the observations mentioned in the introduction.

Figure 8. Evolution of the zone affected by the reoxidation in a TISULC grade.

Then, very rapidly, the system evolves towards a transient state (Figure 9): at 0.7 s, the mixed oxides zone is entirely composed of Al and Ti oxides (including the reoxidation source) and at 2 s, all the inclusions are transformed into alumina. The trace left by the reoxidation event in the steel can be clearly seen in the right-hand side diagram: a spherical shell containing a very high density of inclusions (materialized by a peak in the figure with a maximum of \( \approx 14 \text{ kg/t of alumina} \)). Without steel movement, the shell will be very stable since the O and Al gradients — which are the “driving forces” of any evolution — are very flat. With such a high density of inclusions, a sintering phenomenon between the alumina particles cannot be excluded (all the more since these inclusions went through a liquid state before being transformed into solid).

Figure 9. Final evolution of the zone affected by the reoxidation in a TISULC grade.

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COMPARISON BETWEEN AL-KILLED STEEL AND TISULC STEEL

For the sake of comparison, the model has been run with the same composition as the TISULC grade but without Ti. Similarly to what has been presented in Figure 8, Figure 10 shows the evolution of the inclusions composition during the first moments of the reoxidation. The compositions of the mixed oxides are of course different: they do not contain any Ti and therefore are richer in MnO and SiO₂. The maximum extension of this zone of oxides is similar for the 2 grades. The calculation also shows however that the transformation of all the inclusions into alumina is a little bit faster for the Al-killed steel.

As for the TISULC grade, a transient (almost permanent) state is very rapidly reached and, as for the TISULC grade, the trace left by the reoxidation is a spherical shell with a high density of alumina particles but this shell is very different from the one obtained in the TISULC grade (Figure 11): it is “wider” and its maximum density is 3 times lower (≈4 kg/t compared to ≈14 kg/t). We could imagine that this kind of cluster is less prone to a sintering phenomenon and can be more easily dispersed in the liquid steel flow than the cluster formed in TISULC grades.

As a conclusion, it is believed that the dense, narrow alumina spherical shells formed by reoxidation in TISULC grades give birth to the veils whereas, in Al-killed steel, the more dispersed and spread shells give birth to what are commonly denominated as “alumina clusters”. Because of their densities and cohesion, the veils should be more easily at the origin of castability problems for example when stuck against CC refractory walls.

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EFFECT OF THE AL CONTENT

Calculations have been run with a TISULC grade with a higher Al content 0.05% (other elements having the same content as above). Comparison between Figure 8 and Figure 12 shows some differences during the very first moments of the reoxidation. When Al increases:

- No TiN zone appears. The higher Al content reduces the amount of Fe oxidized in the first cells and therefore the increase of their nitrogen contents.
- The zone containing the mixed oxides gets smaller.
- The reoxidation source is reduced faster.
- … and, consequently; the steady state is reached – when all inclusions are alumina and Al and O gradients are (nearly) flat – sooner.

![Comparison of reoxidation zones](image)

Figure 12. Evolution of the zone affected by the reoxidation in a TISULC grade with 0.05%Al.

Figure 13 clearly shows the consequence of the Al increase: the alumina build-up formed in the steel is denser (and a bit narrower). From this point of view, a too high ratio Al/Ti does not seem to be beneficial in terms of castability.

![Alumina build-ups](image)

Figure 13. Oxygen and Al gradients and alumina build-ups in TISULC steel with 0.05% Al (left) and 0.03% Al (right).

EFFECT OF THE OXYGEN CONTENT

Figure 14 compares the effect of a less intense “reoxidation” intensity than the case presented before (see Figure 9 or Figure 13 right for example). The case referenced “O 54 ppm” in the figure represents an amount of O brought by reoxidation half of the “reference” case “O 89 ppm”. Decreasing the reoxidation intensity results in an alumina shell of smaller diameter and of smaller intensity.

![Oxygen and Al gradients](image)
DISCUSSION AND CONCLUSIONS

A model solving Fick equations combined with inclusion precipitation in composition gradients gives some clues about the origin of the oxide “veils” observed in TISULC grades and therefore about the origin of differences of castability observed between these grades and Al-killed grades.

In this model reoxidation is simulated by “putting” a pure FeO spherical droplet in the middle of a spherical metallic domain. It shows that reoxidations result in the transitory formation of layers of complex mixed oxides whose composition vary rapidly with time getting successively enriched in Mn, Si and Ti oxides when going further from the reoxidation source and when time goes on.

Very rapidly, a quasi-permanent state is reached leaving a spherical build-up of alumina particles at some distance of the reoxidation source. This build-up is much denser in the case of the TISULC grade than for the Al-killed grade. The higher density of particles makes the build-ups prone to sintering (all the more since they went through a liquid state before being transformed into solid), which makes them also much more difficult to be dispersed in the liquid steel flow. Of course, the later in the steelmaking process these build-ups are formed, the more harmful they are since the probability for them to have time to float out is reduced.

Increasing the Al/Ti ratio also results in increasing the build-ups density (but also reducing a little bit its dimension). So, from this point of view, it does not seem to improve the castability. However, it does not mean that, when considering the whole steelmaking process, increasing the Al content is not finally beneficial since, for example, a high Al content could prevent the precipitation of mixed Al-Ti oxides during Ti additions.

Finally, it must be underlined that the numerical values presented in this report depend obviously a lot on the input data: the composition of the steel, of course, but also on the dimension of the reoxidation “sources” which by nature must be very much variable. Furthermore, some physical data may not be very well known as diffusion coefficients and phenomena like inclusion nucleation and growth are not considered since inclusion precipitation are assumed to be taking place at equilibrium.

Generally speaking, the results presented in this report also show that the consequences of reoxidation phenomena cannot not be apprehended only by thermodynamic and mass balance considerations. Typically, such simple approach would not able to explain castability problems encountered in some cases for high Al steels.

REFERENCES