UNDERSTANDING THE ROLE OF MOULD SLAG AND SLAG FILM IN SURFACE QUALITY OF CONTINUOUSLY CAST SEMIS

B. Stewart, M. McDonald, M. Hopkins, R. Burniston,

It is accepted that the majority of surface defects in the continuous casting process originate at, or within 25 mm of, the meniscus in the mould. Whether the defects propagate into cracks is dependent on the heat transfer down the remainder of the mould and events and conditions at and below mould exit. One major influence at the meniscus and down the mould is the performance of the mould flux in terms of its melting, lubrication, solidification and transformations. The formation of slag film between the solidifying shell and the copper mould plate is critical in terms of lubrication and heat transfer, both of which are influenced by its thickness and degree of crystallisation. The films are usually only two to four millimetres thick, but the temperature difference between one face and the other can be 950 °C. Varying the glass/crystalline ratio of the solid part of this film, has a significant and important effect on lubrication, heat transfer and thereby surface quality. This paper describes current and recent work to understand the role of mould slag and slag film in the surface quality of continuously cast semis within Corus UK.

KEYWORDS: mould flux, slag film, heat transfer, surface quality, microscopy

INTRODUCTION

A target of all continuous casting operators is the ability to cast all grades free of surface defects. This will have two advantages; the ability to hot connect a greater proportion of semis to the reheating furnaces and a reduction in the requirement for surface rectification of the as-cast semi and/or rolled product. Research to achieve the target of zero surface defects includes initial solidification, novel mould technology and optimisation of mould operations and secondary cooling. Mould powders are key to the control of initial solidification and optimisation of mould operations. Although a great deal of historical investigative work has been undertaken on the factors associated with mould powders and their influence on surface quality, there is still a great deal of knowledge required on their performance, especially lubrication and heat transfer, to enable their optimisation for the achievement of a defect-free semi.

Mould powders that are added to the mould melt and the resulting slag flows between the meniscus and the copper mould to form a thin layer or film between the solidifying steel shell and the oscillating mould. In the mould-strand gap, the film starts to solidify and, where the chemistry dictates, transforms from a glassy to a crystalline structure. This slag film has two functions lubrication and heat transfer. Uniform and consistent lubrication and heat transfer are required for optimum surface quality, especially for crack prone steel grades, such as those in the peritectic carbon range. It is well known that the ability to perform these functions depends on the mould powder properties, such as composition, crystallisation tendency, melting range, melting rate and the casting conditions; steel grade, superheat, casting speed and alumina pick-up. The aim of the mould powder investigator is to tune the powder properties to suit the casting conditions. This is not always straightforward and the need for compromise is illustrated by the relationship between slag solidification temperature, heat transfer and lubrication. Slag films with low solidification temperatures offer excellent lubrication and rapid shell growth for sticker-prone grades, but the high heat transfer rates exhibited by these films can lead to longitudinal cracking in other steel grades.

Work is being carried out at Corus to improve the surface quality of continuously cast semis through the development and understanding of the events and conditions at the meniscus that affect slag infiltration and conditions in the mould-strand gap resulting from the properties of the slag film. Industrial trials and laboratory studies involving the characterisation of mould powder behaviour, slag films, slag rims and surface quality are being carried out in order to define operational windows for lubrication, mould heat transfer and shell growth and thereby good surface quality. Much of the work is being...
The holes were approximately 50 mm long, 20 mm wide and were interlinked with strands of slag film. These strands of slag film were possibly similar to the ‘rails’ of film reported by Linez for billet casting [5]. The holes were orientated with the longest dimension vertical and were of a tear drop/lozenge shape. It was not possible to see whether the slag films on the other mould plates of strand 6 or of strand 5 displayed the same structure. Casting of the remaining ladles had to be rescheduled, resulting in the two ladle sequence, Trial 14. During the cap-off procedure for Trial 14, it could be seen that the slag film was continuous. Film thickness could not be determined but the film appeared to be as would be expected. Transverse slices of as-cast slabs, 200 mm deep, were obtained to determine whether the slag film observations could be linked to the as-cast structures that were produced. Metallographic analysis was used to investigate the shell development profile, surface quality in terms of longitudinal and transverse cracking and the nature of the oscillation marks. It was found that shell thinning was present, and may occur more, in samples from Trial 13 and the first ladle of Trial 14 than in the samples from the second ladle of Trial 14. It could be inferred from these results that the slag film in the first ladle of Trial 14 was in a similar condition to that in Trial 13, but became more uniform during the casting of the second ladle. It would be expected that as the slag film becomes more uniform, control of heat transfer improves and a more uniform steel shell will develop.

If it is assumed that the slag film in the first ladle of Trial 14 was indeed in a similar condition to that in Trial 13, then since the slag film observed at the end of the second ladle of Trial 14 was observed to be continuous, it follows that the slag film must become continuous at some point during casting of the second ladle. In order to determine just how long it takes for the film to become continuous, the heat transfer to the mould cooling water, \( \Delta T \), and mould thermal monitoring thermocouple temperatures have been analysed. Analysis of the mould water \( \Delta T \) values shows that in Trial 13, \( \Delta T \) is still increasing when the cast is stopped after 44 minutes, Fig. 1. An explanation for the increase in \( \Delta T \) with time is proposed below. Where the slag film is present, heat transfer from

<table>
<thead>
<tr>
<th>Powder B</th>
<th>Powder C</th>
<th>Powder E</th>
</tr>
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<tbody>
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<td>0.94</td>
</tr>
<tr>
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<td>36</td>
</tr>
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<td>CaO+MgO</td>
<td>38.5</td>
<td>35</td>
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<tr>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
<td>5.25</td>
<td>4.25</td>
</tr>
<tr>
<td>Na\textsubscript{2}O+K\textsubscript{2}O</td>
<td>5.25</td>
<td>6.5</td>
</tr>
<tr>
<td>Fe\textsubscript{2}O\textsubscript{3}</td>
<td>1.25</td>
<td>1.25</td>
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<tr>
<td>MnO</td>
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</tr>
<tr>
<td>C\textsubscript{free}</td>
<td>4.75</td>
<td>6.5</td>
</tr>
<tr>
<td>F</td>
<td>5</td>
<td>5.25</td>
</tr>
<tr>
<td>Viscosity at 1300°C</td>
<td>2.7</td>
<td>3.8</td>
</tr>
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**Tab. 1** Approximate average powder compositions based on supplier’s information.

Composizioni medie approssimative di polveri, basate su informazioni del fornitore.

per piastre strette osservato nelle prove 13 e 14.

**Fig. 1** Increase in mould water temperature for narrow plates observed in Trials 13 and 14.

Aumento della temperatura dell’acqua nella lingottiera per piastre strette osservato nelle prove 13 e 14.
the steel strand to the mould will be high. Where there is no slag film in the ‘holes’, the shell and mould will be separated by an air gap and heat transfer will be much lower. Hence as the holes become filled with slag, the heat transfer to the mould will increase, leading to an increase in $\Delta T$. Once complete coverage has been achieved, the slag film will start to get thicker and heat transfer will decrease. Thus, all other casting parameters being equal, it could be expected that the point at which the slag film becomes complete, corresponds to the maximum value of $\Delta T$. In this case, sixteen minutes into the second cast. Hence it has taken eighty minutes from the start of casting for a complete slag film to form. In the meantime, the heat transfer conditions ‘seen’ by the strand on travelling through the mould could be expected to have been very variable. Although the temperature signals from the MTM system show some reduction in variability after ninety minutes, the improvement is not a marked one.

The amount of cracking found on the samples was very limited and there was no evidence to suggest that one sample was worse than another. All the narrow face samples displayed a degree of very fine network, or spongy, type cracking. Maximum crack depths were around 0.5 mm. Mould slag infiltration may be expected to influence oscillation mark formation. The oscillation marks observed were mainly hook-type but there were some fold-type present. There was no clear trend in the oscillation mark formation type from cast-to-cast. These results suggest that the time taken to develop a continuous slag film from Powder E has not had a detrimental effect on the as-cast slab surface quality.

ANALYSIS OF SLAG FILMS

The opportunity to obtain samples of mould slag films from industrial casters is critical to the success of this work. Historically slag films were obtained at British Steel/Corus UK by either dropping the mould level during casting and removing a small sample from near the meniscus, removing slag rim samples from the mould with some slag film attached or catching fragments in a wire basket placed below the mould. However, due to the findings that most defects originate at or near to the meniscus, removal of slag films and slag rims from the mould is no longer permitted during casting. Also, the new safety enclosure around the strand below the mould exit, makes it difficult to collect fragments as they fall out of the bottom of the mould. More recently Corus have followed the example of O’Malley and Neal [6], Hoili[7,8] and Bezerra [9]. By catching the slag film as it falls off the mould walls during cap-off, it has been possible to obtain a significant amount of material. Although no film samples could be obtained at the cap-off of Trials 13 and 14 described above, large samples have been obtained for trials of other powders. The films have been characterised using a variety of techniques and the results obtained could help in understanding the mechanisms of slag film development.

Physical appearance

It was immediately obvious from visual inspection that there were considerable differences between slag films generated by different powders and also between films generated by the same powder in different sequences. Consequently, the first stage in characterising these films was to photograph them. Fig. 2 and 3 show the extremes in appearance of the films ob-
tained after casting with powders B and C respectively. Details of the compositions and properties of these powders are given in Tab. 1.

Figure 2a shows a sample taken from the narrow face mould plate after casting with Powder B for seven hours and twelve minutes (Trial 3). This film is covered in a thick shiny glassy layer and it is possible to see small areas of crystallisation developing within the glassy layer. The sample in Fig. 2b was taken from the broad face mould plate after casting for eight hours and thirty-one minutes (Trial 6) and this film appears crystalline throughout.

The extremes in appearance of films from the less basic powder C are shown in Fig. 3. The sample in Fig. 3a was obtained from a broad face plate after 2 hours 52 minutes of casting (Trial 4). The surface layer appeared quite shiny and the uneven coloured stripes of this layer suggest inhomogeneity in the concentration of iron oxides in the film. At the other extreme, the film in Fig. 3b, also from a broad face plate, has a waxy translucent appearance and the colour is much more even. This film was obtained after 4 hours 39 minutes of casting (Trial 7).

Of particular interest for understanding the development of these slag films were the features revealed when the surface in contact with the mould was examined [10]. The ‘mould-face’ of the powder C film in Fig. 3a is shown in Fig. 4a. It can be seen that the surface has folded as the material has been pushed down the mould. On the reverse of the other powder C sample, it can be seen that the surface in contact with the mould has started to break up and fresh liquid slag has filled the cracks formed (Fig 4b). It is expected that the folds or ‘ripples’ are related to the mould oscillation and will lead to air gaps between the film and mould wall. However, in this case the folds are relatively small and evenly distributed.

Hooli has recently reported very similar patterns of surface roughness in slag films obtained after casting stainless steel slabs [11]. He has attributed these ‘wavy lines’ to poor wetting of the liquid slag on the mould face such that the slag attempts to avoid spreading. Spreading then becomes a forced phenomenon which can happen during the downward motion of the mould. According to Hooli, this explanation is only valid for the first layer in the mould and therefore involves the claim that the rippled areas of the slag films obtained at ‘cap-off’ must have persisted from the start of casting. In Fig. 4a it is interesting to note that the material that filled the fractures in the film after the start of casting, has formed a much smoother surface, although some ripples are present, suggesting that either the ripples cannot fully form after the start or that they take a long time to develop during casting.

Examination of the mould face surface of Powder B films (Fig. 5a), reveals a very different situation. There appear to be vertical stripes of crystalline material, with stripes of glassy material in between. Moreover, it would appear that the glassy material is not always in contact with the mould, rather it forms gutters approximately 13 mm wide and up to 1 mm deep. A crayon rubbing of the film has been done to show up the surface topography. The nature of this surface roughness suggests that the Powder B slag film was not all formed at the same time, but rather that ‘stripes’ of slag film formed first and the gaps in between were later filled in with liquid slag which was in full contact with the strand, but only partial contact with the
mould. This type of slag development is similar to that suggested above for Powder E. Mould water temperature increases, \( \Delta T \), were plotted against casting time and, as with Powder E, \( \Delta T \) increases throughout the first ladle, peaked during the second ladle and continued to decrease during the further three ladles. Unfortunately, analysis of the \( \Delta T \) values for Powder C films indicate that more trials are needed to identify trends.

It is known from studies of the compression of rock layers in the earth's crust, that the thinner the layer being compressed, the greater the number of ripples formed [12]. The depth of the air gap channels is expected to have a significant influence on the thickness of the slag film. The differences observed here between the films from powder B and C may go some way to understanding the variation in the range of film thickness observed by Ludlow et al in fragments obtained below the mould [13].

Optical microscopy

The next stage of the characterisation was optical microscopy. Micrographs of some Powder B films are compared in Fig. 6. These show sections through the thickness of the film. The top of the pictures correspond to the surface in contact with the mould. The photographs are shown to scale and it is thought that the thinner sample was obtained from higher up the mould that the others. Remarkably, in all four films, there is a crystalline region next to the mould and a glassy region next to the strand. In Fig. 6a and 6b, pores are present at the interface between the glassy and crystalline regions. However, the films in Fig 6c and 6d show slightly different behaviour. In Fig. 6c, much of the film is crystalline, and the pores are much smaller and distributed throughout the film. In Fig. 6d, there are two areas of crystallinity and dendrites can be clearly seen on the solidification front.

It is generally thought that when the liquid slag first enters the mould-strand gap, it is quenched against the mould wall to form a glassy layer. Then over time, due to the heat from the strand, the hotter parts of the film close to the strand starts to crystallise, to give a film with a crystalline region sandwiched between the glassy region next to the mould wall and another glassy region due to cooling of what had previously been the liquid lubricating layer. However, this is not the case for the Corus slag films and crystallinity in the film next to the mould has been reported elsewhere [14]. Watanabe [15] has suggested that because the melting point of cuspidine is so high, there is potential for it to form between the shell and mould at very early stages of the process. Also, Li et al [16] have shown that even a temperature as low as 100 °C with a holding time of 10-20 minutes is enough to influence the percentage crystallinity significantly.

Electron microscopy

Hooli has published some very interesting work on the characterisation of slag films using electron microscopy [7,8,11], describing how the layers of slag film build up over time, porosity develops and the slag film breaks up and drops out of the mould. The existence of five layers within the films was reported:

i. a layer formed ‘tailout’ or ‘cap-off’  
ii. a thin layer on the strand shell side, which was possibly the liquid lubricating layer  
iii. a layer with high calcium content  
iv. a layer with high aluminium content with pores  
v. a layer with high sodium and fluorine content as a first layer against the mould.

In the current work, Corus have carried out similar measurements to determine whether the same is true for slag films taken from their plants. Hooli measured the composition of his samples at 100 μm intervals along a line through the thickness of the films using Scanning Electron Microscopy and EDS analysis. The five layers reported were visible in a plot of chemistry against distance from the mould face. In the current
work, SEM/EDA analysis was used to determine the composition of 50 μm x 50 μm areas at 50 μm intervals through the thickness of the films.

The plots for the Powder C films were all very similar and an example obtained for a Trial 4 film can be seen in Fig. 8. The key features are:

- A relatively high degree of variability in calcium content; up to 10wt% over 150 μm.
- Below approximately 800 μm from the mould wall, the fluorine content increases.
- Alumina content peaks at approximately 800 μm from the mould wall.
- The sodium content loosely mirrors the alumina content. It is highest in the region closest to the mould and also around 800 μm from the mould wall. However, although the ‘baseline’ sodium levels are similar to those in Hooli’s film, the step changes are not as dramatic.

- A small step change in silica content at approximately 800 μm from the mould wall.
- A layer at over 1550 μm from the mould wall which appears to be more homogeneous than the rest of the film, particularly with respect to calcium. This could correspond to the layer that Hooli proposes is formed during tail out or cap off or was the liquid lubricating layer when casting stopped.

Five different trials were carried out using Powder B. Most of the films obtained showed similar variation in composition to that shown for a Trial 6 film in Fig. 9a. The key features for this film are:

- The variability in calcium is much less than in the Powder C film.
- The silicon content changes very little.
- Changes in Na content again mirror changes in Al, but the magnitude of these changes is less than in the Powder C film.
- There is some fluctuation in fluorine content and this is the mirror image of the changes in Na and Al. Fluorine is approximately 2wt% lower close to the mould wall than at the side that had been in contact with the strand.
- Beyond 2100 μm from the mould wall there is very little change in the concentration of any of the elements and this may correspond to a layer formed at ‘tail out’ or the liquid lubricating layer.

However, a Powder B film obtained from Trial 5, showed a very different distribution of calcium and silicon (Fig. 9b). Up to 800 μm from the mould wall, the silicon content is the same as for Trial 6 film and the average calcium content is slightly higher but beyond 900 μm from the mould wall, the Ca content drops and the Si level increases, such that the contents of these two elements are very similar to each other. The reason for this is not yet clear. There are peaks in the Ca content at 1800 and 2000 μm from the mould wall. These appear to be associated with dips in the Si content, indicating that the Ca and Si are not always bound together in a single phase with ratio of Ca wt% to Si wt% of one. The number and type of phases formed are expected to control the distribution of the elements in the film. It is expected that where there is a single, say glassy, phase, the elements will be distributed homogenously, but where the layer contains a number of phases, the segregation of the elements will depend on the phases formed and also on the sizes of these phases. Areas of 100 μm x 100 μm have been studied at various points across the films. For each area mapped, qualitative analysis was carried out on each phase found to be present. The variability in calcium content in particular can be understood in terms of the sizes of the phases observed in the EDA maps. The BSE micrograph of a Powder C film from Trial 7 can be seen in Fig. 10 and the six areas mapped are indicated. Area 1 corresponds to the region close to the mould wall, where the variability in Ca was lower. There are two main phases present in this area, a crystalline phase (cupsidine) and a glassy phase. The cupsidine crystals are evenly distributed relative to the 50 μm x 50 μm area used in generating the plots of element concentration through the thickness of the film. The number and type of phases formed are expected to control the distribution of the elements in the film. In contrast area 4 shows much larger expanses of glassy matrix between the crystals. Three different phases were observed and although the silicon content varies from 35.6% to 45.3%, this is not as marked as the difference in calcium between the phases, which ranges from 18.9% to 64.4%.

CONCLUSIONS AND FURTHER WORK

The Corus slag films show some similarities to but also some differences from the Outokumpu slag films reported by Ho-
All of the films obtained in this work exhibited a crystalline region next to the mould. By obtaining much larger samples of mould slag film than were previously available within Corus UK, it has been possible to identify two different types of roughness in the slag film surfaces which were in contact with the mould. In order to explain these observations, two different patterns of initial slag film generation have been proposed:

In the first case, the slag is forced into the top of the mould strand gap as a continuous layer. A thin uniform layer in contact with the mould crystallises and as further material is forced in with each oscillation of the mould, the film surface in contact with the mould is compressed to form fine ripples. The depth of these ripples depends on the thickness of the solid slag layer.

In the second case the slag flows more freely into the mould-strand gap, not as a continuous layer as in the first case, but as a lace-like structure which holds the shell off the mould wall similar to the ‘rails’ described previously for billet casting. Initially the holes are filled with air, but as slag continues to infiltrate the mould-strand gap, the holes in the ‘lace’ are gradually filled with slag. The result is a network of crystalline material with more glassy regions in between. Often these glassy regions are not as thick as the neighbouring crystalline regions. Thus channels are formed and it is anticipated that in the mould, these channels will be filled with gas/air.

Further work is underway to determine the implications of the two types of film for lubrication, heat transfer and as-cast surface quality. A thermodynamic study and complementary XRF analysis are being carried out to determine what crystalline phases/seed crystals might be present in the first film that enters the mould-strand gap.

ACKNOWLEDGEMENTS

The authors would like to thank the ERFCs for their financial support of this work through Project RFSR-CT-2005-00012, the slab caster operators at the Corus plants where this work was carried out, Martyn Whitwood for SEM analysis and Neil Hunter and Keith Bain for helpful discussions.

REFERENCES

ABSTRACT

CAPIRE IL RUOLO DELLE SCORIE DELLA LINGOTTIERA E DEL FILM DI SCORIA NELLA QUALITÀ SUPERFICIALE DI SEMILAVORATI COLATI IN CONTINUO

Parole chiave: acciaio, colata continua, qualità, microscopia

È un fatto accettato che la maggior parte dei difetti superficiali nel processo di colata continua hanno origine in corrispondenza del menisco della lingottiera, o al massimo entro 25 mm da esso. Il fatto che i difetti si propagino in cricche o meno dipende dal trasferimento di calore verso il resto della lingottiera e da eventi e condizioni in corrispondenza e al di sotto dell’uscita dalla lingottiera. Uno dei fattori con maggiore influenza al menisco e al di sotto della lingottiera è il comportamento del flusso nella lingottiera in termini di fusione, lubrificazione, solidificazione e trasformazioni. La formazione di film di scorie tra la superficie di solidificazione e la piastra di rame della lingottiera è critica in termini di lubrificazione e di trasferimento di calore, che sono entrambi influenzati dal suo spessore e dal grado di cristallizzazione. I film solitamente hanno uno spessore solo da due a quattro millimetri, ma la differenza di temperatura tra una faccia e l’altra può essere di 950 °C. Variando il rapporto tra stato vetroso e cristallino della parte solida di questo film, si ottiene un effetto significativo e importante sulla lubrificazione, sul trasferimento di calore e, quindi, sulla qualità della superficie.Questo documento descrive lavori in atto e recenti per capire il ruolo delle scorie nella lingottiera e dei film di scoria sulla qualità superficiale di semilavorati colati in continuo all’interno di Corus UK.