4th International Conference on Molten Slags and Fluxes, 1992, Sendai, ISIJ

# THE DEGRADATION OF SUBMERGED ENTRY NOZZLES

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Synopsis: The degradation of graphite bonded zirconia refractories by mould flux was investigated at 1520°C in an induction furnace which simulated the same flow pattern and stirring velocity that occurs within a continuous casting mould. The results revealed that oxide dissolution was the rate limiting step and that there was no evidence of steel being in contact with the refractory. Particles of undissolved zirconia within the slag increased the effective viscosity resulting in the formation of a viscous slag. Carbon and silicon pickup of the metal were monitored and carbon pickup was found to give a qualitative measure of attack. Silicon pickup was found to be independent of attack.

Key Words - Zirconia/graphite, Submerged entry nozzles, flux line attack.

## 1. INTRODUCTION

A major source of steel contamination and quality deterioration is the reoxidisation of the steel stream from the tundish to the mould. To prevent this reoxidisation, a Submerged Entry Nozzle (S.E.N.) in conjunction with a mould flux provides the necessary physical shrouding. The S.E.N. has an isostatically pressed alumina graphite body with zirconia graphite inserts or 'Z' bands which are in contact with the mould flux when casting.

The mould flux, interacts with the S.E.N. creating a region of local corrosion at the flux/metal interface, limiting the life of the nozzle. The authors have developed a technique to study the degradation of graphite bonded zirconia refractories (14%C, 10%$SiO_2$, 69%$ZrO_2$,) in contact with flux (33%$SiO_2$, 30% CaO+MgO, 10% $Na_2O$, 5%$Al_2O_3$, 2%$Fe_2O_3$, 5%C, 5%F), and liquid steel at 1520°C.

Slag line attack has been the subject of many investigations with most suggesting a cyclic mechanism. Shikano [1] et al proposed that where the refractory contacts the slag, $ZrO_2$ can dissolve in the slag, whilst if steel is in contact with the refractory, carbon will dissolve, exposing zirconia. Since the zirconia cannot be wetted by the steel, the flux will wet the refractory and dissolve $ZrO_2$ exposing graphite, and the process starts over. Mukai [2] et al proposed a somewhat similar mechanism, and also proposed that the dissolution of oxides from the nozzle into the slag film was the rate controlling step.

Hauck and Potschke [3] proposed that the wear was governed by the dissolution of carbon in the slag. At the nozzle/slag/metal interface the carbon dissolved in the slag reacts with the FeO producing iron and carbon monoxide. This reaction produces gradients in the interfacial tensions and hence initiates interfacial convection with the effect of increasing the mass transfer resulting in the formation of a corrosion groove. Mills [4] concluded that this difference in interfacial tension gave rise to Marangoni flow and was the dominant factor in the erosion of the S.E.N. However Marangoni flow is of the order of cms per second, whilst the stirring velocity within a continuous casting mould is an order of magnitude greater. The authors believe that any surface tension driven flow would be negligible in comparison with the imposed flow in the mould.

Hiragushi [5] et al proposed that small particles of zirconia from the S.E.N. enter the slag and increase the viscosity creating a locally inert slag film adjacent to the S.E.N.. This leads to a reduction in the mass transport of $ZrO_2$ entering the slag, and hence a lower rate of attack.

## 2. EXPERIMENTAL

The flow pattern within a conventional mould is illustrated in Fig. 1. On exiting the nozzle, the steel is forced in a circular fashion to the top of the mould to encourage inclusions to dissolve in the flux. The steel, perhaps accompanied by some mould flux, is drawn in a downward motion past the zirconia/graphite 'Z' band with a velocity of about 0.2–0.5 $ms^{-1}$. By using an induction furnace it is possible to simulate not only the flow pattern but also the stirring velocity, as shown in Fig. 2.

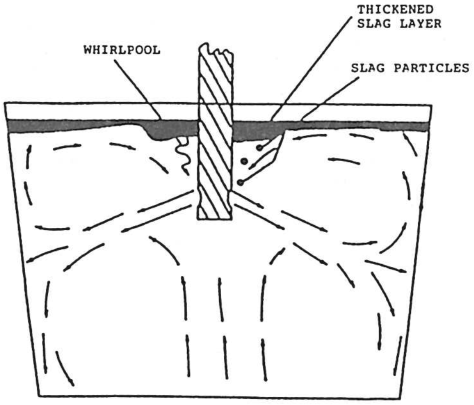

Figure 1 Stirring pattern in mould

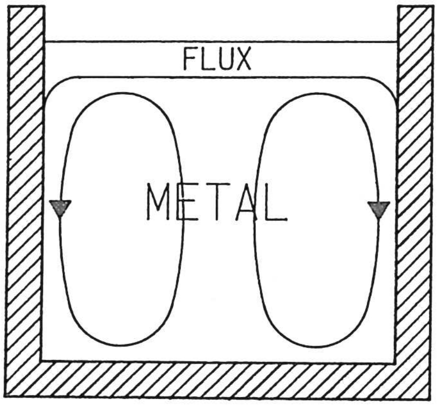

Figure 2 Stirring pattern in experiments

3kgsteel (%C 0.44, %Si 0.24, %Mn 0.84, %P 0.024 and %S 0.004) was placed within the crucible (18cm high, 10⌀). An argon blanket was maintained throughout the experiment, including the melting period. When the metal was at 1520°C, 50g of mould flux was added. 50g was then added every 15 minutes. When the experiment was completed, the crucible was allowed to cool under argon. The crucible was then removed, sectioned and detailed metallographic analysis performed .

In order to follow the chemical reactions occurring, steel samples were taken at various time intervals, and analysed for carbon using a non-aqueous titration technique, and for silicon by atomic absorption spectrometry.

Experiments were done with and without flux, with a fully decarburised flux, and, for comparison, with an alumina/graphite crucible.

## 3. RESULTS

Table 1 shows that alumina/graphite is more severely eroded than zirconia graphite, and that where the refractory was exposed to steel only, the attack was minimal.

Metallographic examination of all experiments where mould flux was present revealed that the maximum wear occurred around the flux/metal/refractory interface, and evidence suggests that this wear extended well below the 3 point interface, although to a far lesser extent.

A strongly adherent slag layer was also revealed, this extended form slightly above the proposed flux/metal/refractory interface and covered the wall and base of the crucible.

Table 1 Erosion measurements

| Material | Erosion depth, mm | Flux |
|---|---|---|
| $Al_2O_3/C$ | >9 | YES |
| $ZrO_2/C$ | 2.5 | YES |
| $ZrO_2/C$ | <0.01 | NO |

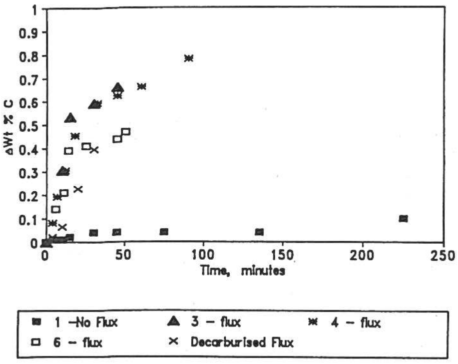

Figure 3 Carbon pickup

Carbon pickup results are shown in Fig. 3. Two interesting features are immediately identifiable. Firstly, with only steel in contact with the refractory, the carbon pickup is minimal throughout the duration of the experiment. Secondly the carbon must be coming from the refractory, as decarburisation of the flux has no effect on carbon pickup.

Fig. 4 shows a surprisingly large silicon pickup. Because the silicon pickup is independent of the presence of mould flux this must come from the refractory. There is about 5% Si in the refractory, and the surface area in contact with the steel is $432cm^2$. Therefore in order for the steel to pickup 0.925% Si, the silicon must be removed from the refractory to a depth of 0.37cm.

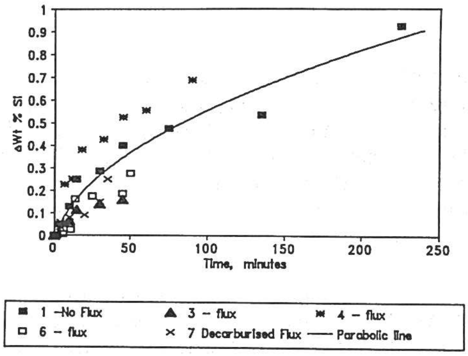

Figure 4 Silicon Pickup

## 4. DISCUSSION

The difference in erosion between $Al_2O_3/C$ and $ZrO_2/C$ suggests that oxide dissolution must be the rate limiting step. If carbon dissolution had been rate controlling, then the two types of crucibles would have corroded at similar rates.

Where mould flux was present, significant wear occured, accompanied by significant carbon pickup. This happened regardless of the presence of carbon in the flux. When no flux was present neither was there erosion or carbon pickup. It is reasonable to assume that carbon pickup is a consequence of, and therefore a measure of, erosion.

In contrast with the behaviour of carbon, the silicon pickup in the steel is indepenent of the presence or absence of the flux, demonstrating that it is independent of refractory erosion. Silicon has to come from within the refractory, and the only way that this is possible is if the silicon is diffusing as SiO, a gas, through the pores in the refractory. The silicon in the refractory is believed to be present as silica, which will react with the graphite to produce silicon monoxide and possibly silicon carbide. Silicon monoxide gas will be able to diffuse out of the refractory and dissolve in the steel. The reactions which control the silicon monoxide pressure are

$$SiO_2 + C = SiO(g) + CO(g) \tag{1}$$

$$\Delta G^o_{1520} = 71{,}643 \text{ J mol}^{-1}$$

and

$$SiO_2 + SiC = 2SiO(g) + C \tag{2}$$

$$\Delta G^o_{1520} = 146{,}955 \text{ J mol}^{-1}$$

The partial pressure of a silicon monoxide calculated from reaction 1, assuming $p_{CO} \approx 1$, is $8.2 \times 10^{-3}$ atmospheres and calculated from reaction 2 is $7.2 \times 10^{-3}$ atmospheres. Therefore the formation of silicon carbide does not drastically reduce $p_{SiO}$. If we consider the chemical reaction step to be fast regardless of whether reaction 1 or 2 applies, the silicon pickup in the metal will controlled by pore diffusion of SiO.

For diffusion of SiO, the instantaneous flux is given by

$$J = \frac{\Delta p_{SiO} D_{eff}}{RT} \frac{1}{X} \tag{3}$$

$\Delta p_{SiO}$ is the difference in $p_{SiO}$ between the bulk refractory and the refractory-steel interface, $(p_{SiO} - p_{SiO,metal})$. $p_{SiO,metal}$ can be assumed to be zero, and therefore $\Delta p_{SiO} = 7.2 \times 10^{-3}$ atmospheres. $D_{eff}$is the effective diffusivity of SiO in the pores of the refractory, R is the gas constant, T is the temperature, and X is the depth of the silicon depleted zone in the refractory.

The experimentally measured quantity was Wt% silicon therefore it is desireable to express the flux of SiO in terms of the change of Wt% silicon in the steel

$$\frac{dWt\%Si}{dt} = J \frac{A\ MW_{Si}}{Wt_{st}} \times 100 \tag{4}$$

by mass balance, for a large diameter crucible:

$$X = \frac{W_{st}\ \Delta Wt\%Si}{Wt\%Si_{ref}\ \rho_{ref}\ A} \tag{5}$$

where A is the surface area of contact between the steel and the refractory, $W_{st}$is the mass of the steel, $Wt\%Si_{ref}$ is the Wt% silicon in the refractory, $\rho_{ref}$ is the density of the refractory, $MW_{Si}$ is the mole weight of silicon, and $\Delta Wt\%Si$ is the silicon pickup in the steel.

Combining equations 3,4 and 5

$$\frac{dWt\%}{dt} = \frac{\Delta p_{SiO}}{RT} D_{eff} \frac{Wt\%Si_{ref}\ \rho_{ref}\ A^2\ MW_{Si}}{\Delta Wt\%Si\ \ W_{st}^2} \times 100 \tag{6}$$

integrating gives

$$\Delta Wt\%Si = \left[ 2\ \frac{\Delta p_{SiO}}{RT} D_{eff} \frac{Wt\%Si_{ref}\ \rho_{ref}\ A^2\ MW_{Si}}{W_{st}^2} \times 100 \right]^{1/2} t^{1/2} \tag{7}$$

which corresponds to the parabolic rate equation

$$\Delta Wt\%Si = k\ t^{1/2} \tag{8}$$

The solid line in figure 6 was determined by fitting the experimental data to equation (8), and k was found to be $8.2 \times 10^{-3}$ Wt%Si $s^{-½}$

A value of $k = 8.3 \times 10^{-3}$ Wt%Si $s^{-½}$ is calculated from equation (7), using $Wt\%Si_{ref} = 4.9$, $\rho_{ref} = 3.5gcm^{-3}$, $A = 432cm^2$, $W_{st} = 3Kg$ and $D_{eff} = 0.7cm^2S^{-1}$, which shows very good agreement with the experiment. The value for $D_{eff}$ was calculated using

$$D_{eff} = D_{SiO-CO} \frac{1}{\tau} \tag{9}$$

where $D_{SiO-CO}$ is the interdiffusivity of SiO and CO and $\tau$ is the tortuosity factor. $D_{SiO-CO} = 3.5cm^2S^{-1}$ [6] and $\tau$ was assumed to be 5, this value, which is reasonable for compacted particles [7].

It therefore appears that the experimental measurements of silicon pickup are consistent with diffusion of silicon monoxide within the refractory being the rate limiting process

Metallographic analysis revealed a slag band adjacent to the wall (Fig. 5) and the base of the crucible. This shows a large number of zirconia particles which have entered the slag and begun to dissolve. Regardless of the duration of the experiment, a continuous coating of flux was found on the crucible and there was no evidence that the steel had been in contact with the refractory, which calls into question the cyclic mechanism proposed by other workers.

The proposal by Hiragushi [5] that small particles of zirconia enter the slag and increase the viscosity creating an inert layer would be supported by the results of this investigation.

The refractory slag interface after 90 minutes exposure (Fig. 5) shows a high density of undissolved zirconia particles within the slag. Examination of a sample which had been exposed for 4 hours showed a higher quantity of undissolved zirconia particles. This would suggest that the corrosion results in the formation of very viscous slag

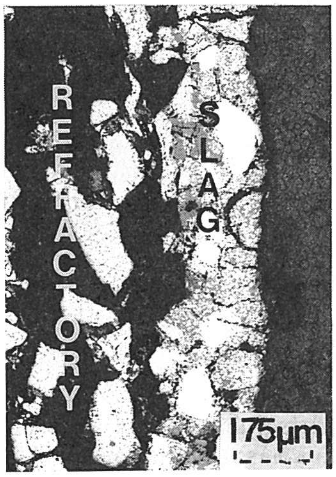

Figure 5 90 minutes exposure.

local to the refractory surface, as there is no evidence of any undissolved particles within the slag on top of the steel. If the slag had a low viscosity, the stirring effect would result in these zirconia particles being carried away into the top slag.

## 5. CONCLUSIONS

(i) Oxide dissolution controls the rate of degradation.

(ii) The combination of mould flux and steel are necessary to produce a wear pattern. Without flux there is no erosion.

(iii) Carbon pickup can be used as a measure of erosion.

(iv) The silicon pickup is independent of erosion since the source of this silicon is the reaction between silica and graphite within the refractory.

## 6. ACKNOWLEDGEMENT

The authors would like to thank S.E.R.C. and Thor Ceramics for their financial support of this research .

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