SCHELLER, P.R. Mass exchange at the metal-slag interface in the continuous casting process. *VII International Conference on Molten Slags Fluxes and Salts,* The South African Institute of Mining and Metallurgy, 2004.

Mass exchange at the metal-slag interface in the continuous casting process

P.R. SCHELLER

Freiberg University of Mining and Technology, Institute of Iron and Steel Technology

Reactions between metal and slag are of decisive importance for metallurgical processing. In the continuous casting process, where metal solidifies at the metal-slag interface, reaction products can cause surface defects, with quality damages of the cast products as a consequence. These investigations are focused on the contact area between casting flux and metal. The samples were taken from the mould during the casting process.

The results show that layers up to approximately 300 nm from the slag/metal interface represent a specific reaction space. Sodium in this layer on the slag side plays a specific role, which is explained on the basis of experimental results. The transport of oxygen near the interface and the charge transfer is explained on the basis of the ionic character of the slag. The mass transfer rate of oxygen crossing the interface is calculated from measured data, and conclusions concerning the stability of the interfacial tension are made.

Keywords: mass exchange, metal slag reaction, interface, ion transport, oxygen transfer, oxidation, casting slag, flux, sodium

Introduction

Casting powders used in continuous casting fulfil various tasks such as preventing air contact, absorbing non-metallic inclusions from the liquid metal, preventing heat losses while still on the liquid metal surface, controlling heat transfer, and providing lubrication at the gap between the strand shell and the mould wall. After the casting powder has melted, it forms a layer of liquid slag on the surface of the molten pool, which then continuously infiltrates the mould/strand gap. It is known that the chemical composition of the slag is changed by the absorption of non-metallic inclusions and reactions with metal [1-3]. Mass transport from the both sides of the interface to the bulk takes place by diffusion, and free and interfacial convection. The interfacial convection contributes significantly to the total mass transport as shown in previous papers [4-7].

This study presents results obtained in basic investigations into mass transfer between metal and slag and how the stability of the interfacial tension is affected by the mass transfer of oxygen through the interface.

Experimental

During industrial casting, samples were taken from the mould as described previously[4]. At this sampling method the whole square section, including liquid steel, liquid slag, sintered and powder layer, is taken in the container with 50 mm diameter and quenched immediately in water. The casts were performed at Krupp Thyssen Nirosta in Bochum works. The cast steel was AISI 304. The temperature of liquid steel in the mould was approx. 1460°C. The chemical composition of the cast steel and of the casting powder in delivered state is indicated in Tables I and II respectively. After quenching, the slag and metal were separated carefully and prepared for further investigations.

The concentration profiles of elements were measured using Secondary Neutral Mass Spectroscopy (SNMS). In this method the respective surface layer is removed layer by layer down to a depth of around 7 μm in the metal and around 3.5 μm in the slag through sputtering. The sputtering rate was approx. 2 nm/s and approx. 0.7 nm/s for metal and slag respectively. The diameter of 4 mm for the sputtered area was used.

Results

Change in the mean chemical composition

The main components of the investigated casting powders are CaO and SiO_2, which make up together approx. 60% of the mass. The relevant physical properties of slags for continuous casting, such as viscosity and surface tension, are adjusted by adding CaF_2, Na_2O, K_2O, Li_2O and FeO, MnO and MgO. Even small additions and changes in composition can have a considerable effect on these properties.

The change in the chemical composition of the slag from 13 samples is plotted as a bar chart in Figure 1. Greatest changes show SiO_2 (decreasing) and TiO_2 (increasing). In the case of casting slag, oxygen is supplied to the liquid metal mainly from (FeO) and (SiO_2), with [Ti], [Mn] and [Cr] being oxidized. (Designation ( ) and [ ] indicates the slag-phase or metal-phase respectively.) The greatest exchange takes place between (SiO_2) and [Ti]. Thermal convective flow, as well as phase boundary convection in the slag layer, decisively influences the mass transport and therefore the distribution coefficient e.g. $\Delta(TiO_2)/[Ti]$ during the reaction time [4-7]. The chemical composition of the mould sample indicated in Figure 1 is representative for slag layer height greater than 6 mm where both kind of convective flows are in action [4-7].

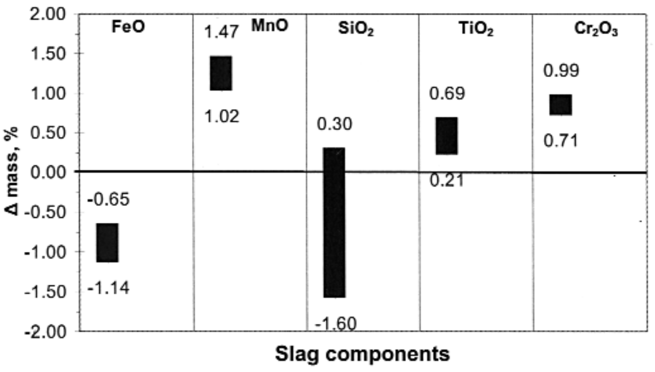

Figure 1. Change in the chemical composition of slag during casting compared to virgin casting powder (C and moisture losses are taken into account)

The results described above show that intense mass exchange between slag and liquid metal takes place.

Conditions at the slag/metal boundary

In further investigations, the concentration of some elements as a function of distance from the phase boundary in the slag and metal was measured using the SNMS-analysis method. The concentration profile of certain elements is discussed in the following on the basis of a sample taken during the casting of AISI 304.

The concentration profile of some elements on the metal side is shown for one representative sample in Figure 2(a). Starting from the bulk of the sample, the oxygen concentration increases up to 10% at the phase boundary. Other surfactants such as sulphur and nitrogen both enrich to approx. 0.6%. A qualitatively similar progression is shown by Al, which is reduced from the slag. Cr, Mn and Ti, by contrast, are subject to strong depletion at the phase boundary, indicating their oxidation and transfer into the slag. On the slag side for the same sample, Figure (2b), the oxygen concentration decreases towards the phase boundary and thus corresponds with the oxygen increase at the interface in the metal phase. A similar curve is shown by Al. The Cr oxidation is reflected in a very high concentration at the phase boundary, which decreases exponentially towards the bulk of the phase. The Ti and Mn concentrations are not uniform but indicate a high amount of pick-up.

The Na concentrations deserve particular mention: at the phase boundary the Na concentration increases to a value of 11% in this sample and up to 35% in other samples with an Na_2O average concentration of around 8% in each slag. Similar profiles were measured in all other samples. Numerical values of element concentration at the interface (after 5 s sputter time) and in larger distances from there (after 3000 s and 4000 s sputter time in the metal and slag phase respectively) are listed in the Table III. Additionally, the measured average element contents in the sample are indicated. These values are used for further calculations, as explained below.

The measured concentration profiles show that, on both sides of the interface, high concentration gradients exist. The thickness of these layers is approx. 150 nm on the metal side and approx. 400 nm on the slag side. The large concentration gradients on both sides of the interface indicate that interface reactions take place quickly. The kinetic of the total mass transfer is therefore determined by

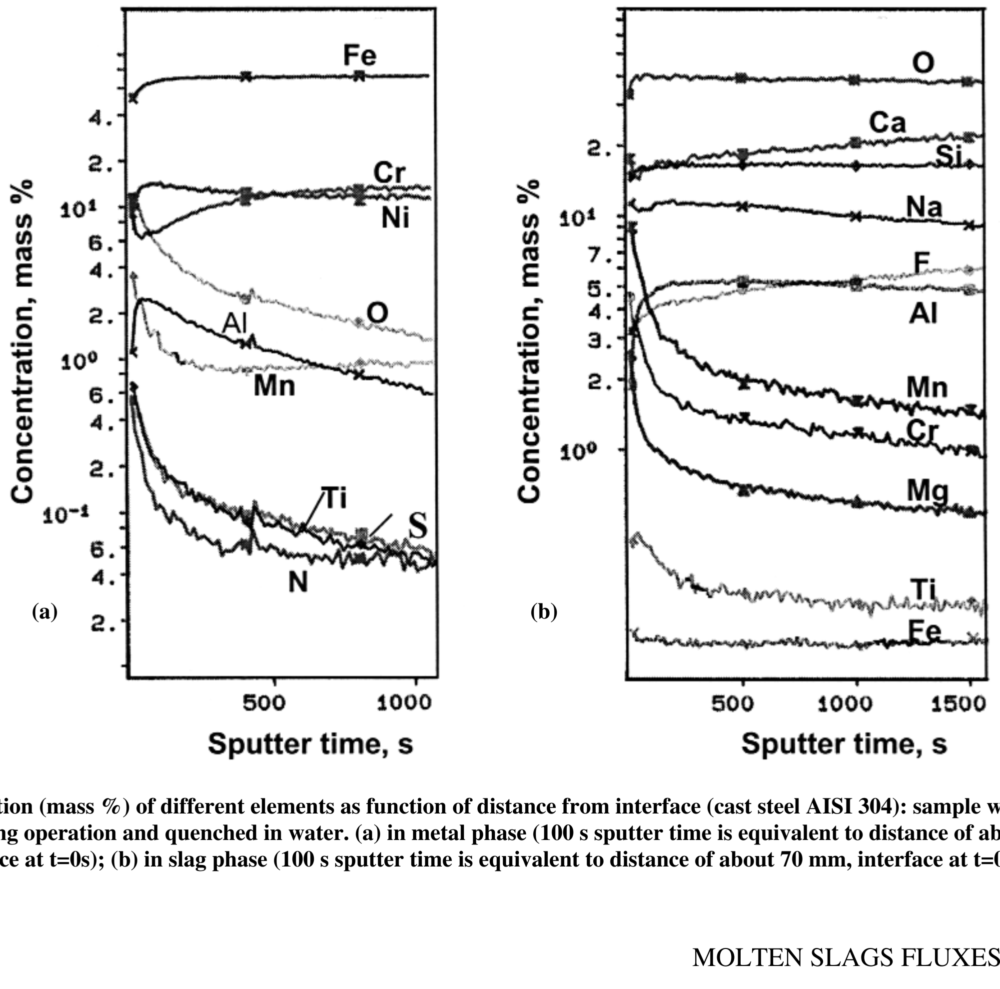

Figure 2. Concentration (mass %) of different elements as function of distance from interface (cast steel AISI 304): sample was taken during continuous casting operation and quenched in water. (a) in metal phase (100 s sputter time is equivalent to distance of about 200 nm, interface at t=0s); (b) in slag phase (100 s sputter time is equivalent to distance of about 70 mm, interface at t=0s)

Table I
Chemical composition of tested steel AISI 304 (Mat. No. 1.4301), mass %

C	Si	Mn	P	S	Cr	Mo	Ni	Ti	Al	Fe
0.038	0.51	1.04	0.028	0.002	18.22	0.33	8.54	0.008	<0.003	bal.

Table II
Chemical composition of casting powder before use. Carbon and moisture losses are already taken into account. In delivery state: C(free) 2.2–2.9%, CO_2 5.5–6.8%.

FeO	MnO	P	SiO_2	Al_2O_3	TiO_2	CaO	MgO	F	Na_2O	K_2O	Li_2O
1.27	0.04	0.04	33.5	7.05	0.14	38.6	0.81	8.40	8.23	0.50	1.08

the transport in the phase with lower convection flow and lower diffusion velocities. The mass transfer through the interface is linked with a reduction in interfacial tension. As shown in previous papers [4-7] the resultant interfacial convection increases the mass transfer. In Figure 3, a square section through the slag/metal interface is shown. Irregularities with depressions are probably caused by movements at the contact area as a result of local fluctuations in surface tension.

Although the average Na_2O-concentration in all slag samples is close to concentration array between 7% and 8%, the recorded concentration profiles of the slag samples show a high enrichment of Na at the interface (till 35%). The possible reactions between the molten steel and slag are:

$$n(Na_2O)+[Ti]\leftrightarrow TiO_x+2n\ \{Na\}\uparrow \qquad [1]$$

$$n(Na_2O)+[Cr]\leftrightarrow CrO_x+2n\ \{Na\}\uparrow \qquad [2]$$

{ } denotes the gas phase. As in the investigated steel melt Na is insoluble, the Na-vapour in the slag layer can react with iron oxide

$$2\{Na\}+(FeO_X)\leftrightarrow(Na_2O)+\left(FeO_{(X-1)}\right) \qquad [3]$$

or it exhausts from the slag and powder layer and can react as listed below:

$$2\{Na\}+\{CO_2\}\leftrightarrow<Na_2O>+\{CO\} \qquad [4]$$

$$4\{Na\}+\{O_2\}\leftrightarrow 2<Na_2O> \qquad [5]$$

< > denotes the solid phase. Considering the reactions [1] and [2] as ionic reactions then the consequence would be a local disruption of polarized layer at the slag side. The attraction and repulsion between the vapour and the surrounded ions cause the instability of interfacial tension and than shear stress, which induce the interface convection.

For further interpretation of the conditions at the interface *on the metal side* the mass balance was calculated (compare Fig. 2a). The mass balance for the analysed oxygen quantity is indicated in Table IV and is based on values from Table III.

In the calculation it was assumed that oxygen exists only in stoichiometric compounds with Al, Ti, Mn, Cr and Fe, as indicated in Table III. The calculation shows that quantitatively main oxide phase is 'FeO' followed by 'Cr_2O_3' with only small fraction of 'TiO_2' and 'Al_2O_3'. Analysing the two-phase diagram Cr_2O_3–FeO one can see that eutectic point at 2.5% Cr_2O_3 exists with the low melting temperature of 1345°C [9,10]. From this finding it follows that, at the interface of the metal phase, a layer with a thickness of approx. 100 nm exists consisting of liquid and possibly partially solid ($FeO\bullet Cr_2O_3$)-oxides in diverging quotes. It should be emphasized that the designation of oxide compounds as above is symbolic because this phase has an ionic character. A smaller part of the metallic interface contains not associated Fe as well as Ni (compare Table III).

At the slag side near the interface there are also different concentration gradients of single elements at the interface, which exist as ions or in sequestered form. The concentration gradients cause, after the Stefan-flow's principal, a convection which is superposed to the ionic migration and diffusion and can slow down or accelerate the flow normal the phase interface. The viscosity of the slag as material property is influenced strongly both by the concentration and by the temperature gradients. Different enrichment, particularly of Na and Mg near the interface, decrease or increase locally the interfacial tension and produce therefore the gradients of interfacial tension.

Stability of the interface

The mass flows on the interface induce changes in the interfacial tension. In the following the flow rate of oxygen ions through the interface is examined. Therefore the

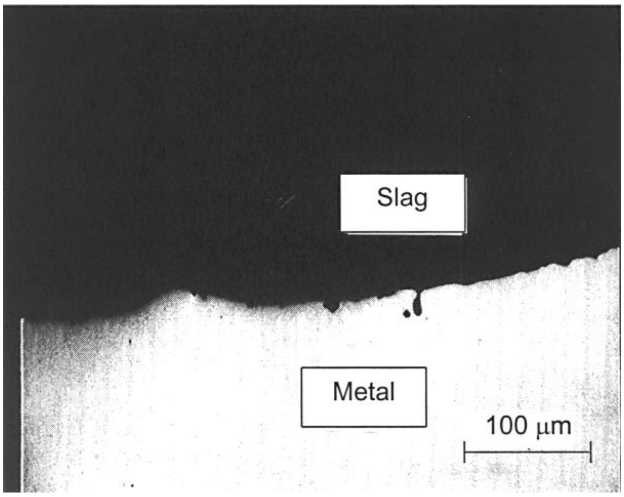

Figure 3. Deformation of the metal-slag interface (interface between metal and slag)

Table III
Element concentration (a) in the metal phase and (b) in the slag phase near the interface (5 s sputter time) and after 3000 s and 4000 s sputter time. Additionally, the average element content in the sample is indicated

(a)

Sputter time	Element content, mass %									
	N	O	Al	P	S	Ti	Cr	Mn	Fe	Ni
t=5s	0.54	10.9	1.2	0.07	0.45	0.66	9.6	3.4	50.3	10.5
t=3000s	0.04	0.35	0.11	0.036	0.023	0.016	14.1	1.1	73.4	11.2
Aver. value per sample	0.027	0.006	0.003	0.017	0.002	0.009	18.18	1.05	-	8.98

(b)

Sputter time	Element content, mass %										
	O	F	Na	Mg	Al	Si	Ca	Ti	Cr	Mn	Fe
t=5s	33.3	4.5	11.4	2.5	1.9	15.2	17.5	0.4	3.3	8.9	0.2
t=4000s	36.4	7.4	6.4	0.4	4.0	16.5	27.4	0.2	0.7	1.1	0.2
Aver. value per sample	35.9	7.6	6.1	0.4	3.8	15.7	26.6	0.2	0.7	1.0	0.2

changes in the chemical composition of the slag layer are compared to the initial state as an indicator for mass transport through the interface layer.

In the following treatment it is assumed that in the present experiments the separation of non-metallic inclusions from liquid metal into the cast slag does not play an important role. The amount of absorbed metal oxide in the slag originates therefore from the oxidation of metal caused by transfer of oxygen ions from the slag into the metal-phase,

$$[Me]+\left(O^{2-}\right)\leftrightarrow(MeO)+2e^{-} \qquad [6]$$

whereas different a oxidation level depends on the activity of the ions. The average amount of absorbed Me-oxide in the slag in the investigated samples is as follow: TiO_2, Cr_2O_3 and MnO with 0.4 mass %, 0.9 mass % and 1.25 mass % respectively. The oxygen in these oxides was delivered particularly from slag components SiO_2 and FeO and reacted with elements of metal phase. The other main components of the slag with their mass fraction are listed below:

SiO_2 33%; CaO 38%; Al_2O_3 7 %; F 8%; Na_2O 8%

On the basis of these data, the average molar mass flow of oxygen $\dot{n}_0$ through the interface is calculated as an example; furthermore, slag with the density of 2.6 g cm^{-3}, layer thickness of 10 mm and the maximum residence time (equivalent to the reaction time) on the surface of the liquid metal of 500 s (derived from powder consumption data [4]) was assumed. With these data the molar mass flow of oxygen is calculated as = $\dot{n}_0$ $4.8 \cdot 10^{-5}$ mol cm^{-2} s^{-1}. This value is lower than the minimum one declared by Riboud and Lucas[11] (10^{-5} mol cm^{-2}s^{-1}), whereas the interfacial tension between metal and slag (Fe-Al and CaO-SiO_2, inert atmosphere) is decreased to zero.

In practical operations $\dot{n}_0$ has a higher value because a maximum reaction time is presumed in the calculation. Previous investigations show that the slag layer is well mixed in the bulk [8] and the equilibrium distribution between slag and metal is reached up to 14 mm slag layer thickness[5]; this indicates a high reaction rate.

Discussion

For the description of the mass transport through the interface, it is important to indicate that there exists an Fe-depletion on the metal side and an Fe-enrichment on the slag side in all samples. Therefore the oxygen transport through the interface could be explained as below:

The migration of O^{2-}anions in the slag is very slow due to their big diameter but the migration of Fe^{2+}-ions are much higher [12]. For Fe^{3+}-ions it is assumed that they are implemented in silicate networks, thus these ions are rigid. The self diffusion coefficient of Fe^{2+} in CaO-FeO-Fe_2O_3-SiO_2-slags ($x_{CaO}/x_{SiO_2} = 0.79$) with 10% of (FeO+Fe_2O_3) is $D_{Fe^{2+}} = 7 \cdot 10^{-9}$ m^2/s [13] at 1600°C. It is increased due to fluorite-ions as well as Ca^{2+}-ions [14]. The depletion of Fe near the interface in the metal phase can be explained by enrichment of oxygen. On the other hand, the enrichment of Fe near the interface in the slag phase is caused by back diffusion of Fe^{2+}-ions after giving oxygen as Fe^{3+}-ions into the molten metal. They uptake oxygen from the other slag components (e.g. from Na_2O by production of $(NaFe)^{4+}$-cations with tetrahedral structure implemented in silicate network [15]). They give oxygen into the molten metal at the interface again or are reduced by Cr or Ti. In this way, recirculation flow of iron ions near the interface is established.

In the investigated slag the concentrations of O, Na and F are very high at the interface. On the metal side the concentration of O, Cr and Ti are high and that of Fe low. This indicates a higher concentration of ion complexes. The charge exchange takes place in this case by electron conduction, as has been shown for oxygen transport in FeO_n-CaO-SiO_2-slags placed on molten iron [16].

Table IV
Balance for oxygen at the metal interface (after 5 s sputter time). Assumption: Al, Ti, Mn and Cr exist in stoichiometric compounds as 'Al_2O_3', 'TiO_2', 'Cr_2O_3' and the rest of the oxygen exists as stoichiometric compound 'FeO'

Element	O	Al	Ti	Mn	Cr	Fe	Fe_{free}
Concentration at the interface, mass %	10.9	1.2	0.66	3.4	9.6	50.3	24
Fraction of O as 'MeO' compound, %	-	5	4	9	41	41	-

Conclusions

From the investigations performed on the steel grade AISI 304 and the slag for continuous casting, the following conclusions can be derived:

- i) On both sides of the slag/metal interface high concentration gradients of all elements exist. The degree of gradients depends on the elements. The highest concentration gradients exist in the range up to approx. 150 nm on the metal side and up to approx. 400 nm on the slag side.
- ii) The adsorption phase enriched with oxygen on the metal side of the interface contains mainly oxygen, iron and chromium ions, which show the stoichiometric relations as FeO and CrO_n. A part of this phase contains Fe and Ni, which are not associated with oxygen.
- iii) The concentration profiles and mass exchange at the interface can be explained e.g. by using the ion theory. The transport of Na-ions to the interface within the slag boundary layer seems to have a strong effect on charge transfer at the interface, which is controlled by electron transmission.
- iv) The estimated molar mass flow rate of oxygen through the slag/metal interface lies in the range of mass flow rate at which the interfacial tension is reduced to zero.

Acknowledgements

The industrial trials and sampling were performed at Krupp Thyssen Nirosta, which is hereby gratefully acknowledged.

References

1. APELIAN, D. and McCAULEY, W.L. *I&SM*, vol. 10. no. 12. 1983. pp. 42-43.
2. EMI, T., NAKATO, H., IIDA, Y., EMOTO, K., TACHIBANA, R., IMAI, T., and BADA, H. *Proc. 61st NOH-BOS Conf.* ISS-AIME Chicago, April 16–20. 1978.
3. MILLS, N.T., BHAT, B.N. *I&SM*, vol. 5. 1978. pp.18–24.
4. SCHELLER, P. R. *Proc. 3rd Europ. Conf. Cont. Casting*, Madrid, Spain, Oct. 20-23. 1998. vol.2. pp. 797–806.
5. SCHELLER, P. R. *Proc. Sixth International Conference on Molten Slags, Fluxes and Salts*. 12–17 June 2000, Stokholm, Sweden – Helsinki, Finland, Session 6, Filename: 405.pdf.
6. SCHELLER, P.R. Surface tension – driven flows in small volume metal melts. *2nd Int. Conf. on the Science & Technology of Steelmaking*. 10–11 April 2001, University of Wales, Swansea, UK, pp. 667–673.
7. SCHELLER, P. R. Interfacial phenomena between fluxes for continuous casting and liquid steel *I&S*. vol. 29. 2002. no. 2. 154–160.
8. SCHELLER, P.R. *Proc. Mills Symposium*, 22–23 August 2002, , London, Great Britain, 487–493.
9. BELOV, B.F., NOVOKHATSKII, I.A., RUSAKOV, L.N., GOROKH, A.V., and SAVINSKAYA, A.A. *Zh. Fiz. Khim*. vol. 42. 1968. pp. 856–858.
10. HOFFMANN, A. *Arch. Eisenhüttenwes*. vol. 36. 1965. pp. 155–623.
11. RIBOUD, P.V., LUCAS, L.D. *Can. Metall. Q*. vol. 20. 1981. p. 199.
12. VYGEN, P., ENGELL, H.-J. *Arch. Eisenhüttenwes*. vol. 40. 1969. pp. 359–365.
13. ENGELL, H.-J., VYGEN, P. *Ber. Bunsenges. Physik. Chem*. vol. 72. 1968. pp. 5–12.
14. TAYLOR, J. *Intern. Symp. Met. Chem. Conf.*, Sheffield.1971. pp. 31–34.
15. TURKDOGAN, E.T. *Physicochemical properties of molten slags and glasses*. The Metals Society, London, 1983.
16. ENGELL, H.-J. *Techn. Mitt.* Krupp, Forsch. Ber. Bd. 24. 1966. pp. 1–7.