

The interfacial convection in fluxes in the continuous casting process

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In this paper the generation of interfacial convection is investigated on the basis of the samples taken in the mould directly in the continuous casting process and quenched in water. Besides of the mass transfer as the result of the chemical reaction, the solidification structure near to the interface with liquid steel was investigated. The results show near to the interface the layered structure containing crystalline and partially glassy layers with the thickness of 50 to 150 μm . They occur as well under the conditions when thermal convection in the flux layer exists as under the conditions when thermal convection does not exist. In each kind of layer a different frequency of crystallisation nuclei were recorded. The reduced iron and chromium oxides produces small metal droplets with $<1 \mu\text{m}$ to $2 \mu\text{m}$ in diameter which act as nuclei for the crystallisation of slag. These oxides are products of the chemical reactions at the flux/steel interface and are transported by the convection into the bulk of flux layer. Their attendance and distribution in partially glassy and crystalline layers contribute to the different solidification structures besides of the thermal layering. The sources for differences of temperature are rapid local heating at the flux/steel interface and cooling at the place of sintered layer fusion in the casting process. In the quenched samples it is a strong cooling at the slag/metal interface. All of these results indicate strongly the existence of the interfacial convection.

KEYWORDS: INTERFACIAL CONVECTION - MASS TRANSPORT - THIN LAYER - CASTING FLUX - FLUX SOLIDIFICATION

INTRODUCTION

In the metallurgical process technique the understanding of transport phenomena is a key knowledge besides of physical chemistry of reactions. As the reactions at interfaces are usually rapid the transport from the interface to the bulk of the reacting phases determines the total reaction rate. Looking to the metal-slag reactions the transport of reactants in the given slag phase limits the kinetics. In e.g. the continuous casting the thin liquid flux layer at the meniscus reacts with liquid steel before it infiltrate the gap between the steel shell and the mould wall. Transport phenomena in the slag phase as thermal and interfacial convection and diffusion determine the reaction rate between both phases. The experimental results presented in this paper focus on the detection of the occurrence of interfacial convection. Furthermore its contribution to the total mass transfer is analysed for the industrial continuous casting process.

Convection flow in the fluid phases have a decisive effect on mass and heat transport. In the case of reactions between the metal and the slag, the flows and the mixing in the slag phase determine the kinetics of the reactions because of higher viscosity (1). Here a distinction can be drawn between large area, thermal convective flows taking place under specific conditions, and convective flows in the vicinity of the interface occurring, for example, finally as a result of chemical reactions at the phase boundary (2).

Gradients of interfacial energy along the interface produce interfacial convection which increases the mass transport within

and through the boundary layers. These gradients can be generated by the gradients of temperature, concentration, electrical potential which in turn are usually caused by local differences of species transfer through the interface and their diffusion. In slag-metal systems such convection reaches high intensity (3-5) because of high values of interfacial energies. In the most of systems the interfacial energy decreases with increasing mass flow rate through the interface of diffusing components. The instability of the interface between two undisturbed and still fluids is therefore depen-

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dent on the quote of the diffusion coefficients in both phases of the passing through component and on the quote of the kinematical viscosities of both phases. Therefore the fluid dynamic controlled instability occurs if e.g. is $D1/D2 = 1$ and $v1/v2 > 1$ (6). These conditions are still fulfilled for liquid slag/metal systems (7). The induced flow generates in this case microwaves at the interface which is termed the Kelvin-Helmholtz instability and was reported in few papers (2, 8-9).

ANALYSIS OF THE PROBLEM AND ITS BASIC DESCRIPTION

Convection Flows

For the problem of interest here relates to how local disruption of the interfacial tension affects the flows in a

$$L_c \Delta \sigma \rho \eta^{-2} \equiv \frac{F_\sigma F_\rho}{F_\eta^2}$$

(1)

where $L_c \Delta \sigma \rho \eta^{-2}$ is denoted the Steinmetz number Ste as derived in the previous papers (2,11). An identical expression is obtained by division of the known numbers Re and We , Re^2/We . By linking the acting forces in the form of the above-mentioned value (equation 1), the overall relationship for convection flows is maintained without flow velocity being a factor.

For an identical disruption of the interfacial energy ($\tau_{max} = \Delta\sigma/\Delta x = \text{constant}$) increasing layer thickness will give a constantly strong impulse at an even greater distance from the disruption. When viewed perpendicularly to the phase boundary, layers further away from the interface are also moved due to friction and the impulse decreases with the distance from the interface. As stated previously, this gradient is the greater, the thinner the layer. For the respective fluid, however, $\text{grad } \tau$ decreases with increasing Ste (because $Ste \sim L_c$ or Δy) and in parallel greater fluid volume near the interface is moved. It is therefore logical to use the Steinmetz number Ste to characterize the flow conditions in thin fluid layers caused by gradients of

slag layer on top of the liquid metal. The details of this analysis are described in the previous papers (2, 7, 10).

The movement of a briefly accelerated volume element or fluid layer is determined by a given interfacial tension force F_σ (corresponding to $\Delta\sigma$) acting as a result of the disturbance in a local area on the interface, the inertia force F_ρ and the viscous force F_η . As the velocity in metallurgical systems cannot normally be measured in experiments at such short distances (movement at the boundary layer), only the variables describing the acting forces and the characteristic length can be considered for a description of the problem (variables L_c , σ , ρ , η).

An analysis of the problem with the aid of the similarity theory gives the following expression to describe fluid movement in the boundary layer area:

interfacial tension.

Mass transport

Three dimension free numbers as Sh , St and Bo , Sherwood, Stanton and Bodenstein respectively, are usually used to describe the mass transfer. With respect to the analysis of the mass transport description discussed in the introduction, the Bo -number is suitable for the description of the problem. For improved evaluation of the measured values the modified Bodenstein number Bo^* is new defined, as the mass flow caused by diffusion cannot be separated from mass flow caused by convection in experimental investigations. It defines the quote of the total (measured) mass flow rate density of analysed species which results from the transferred mass through the interface in the reaction time $\dot{m}_{i,\Sigma}$ to the mass flow rate density caused by diffusion $\dot{m}_{i,D}$

$$Bo^* = \frac{\dot{m}_{i,\Sigma}}{\dot{m}_{i,D}}$$

(2)

If the upper fluid (e.g. slag) is assumed as completely still without any convection so the species i will be transported in this fluid only by the diffusion. If the mass transport is controlled only by diffusion, than is $Bo^* = 1$.

If the interfacial reaction controls the total rate, than is the $Bo^* \leq 1$. Otherwise, if the reaction products or transferred species

are transported away by convection (e.g. thermal or interfacial convection), than is the $Bo^* > 1$. If interfacial convection occurs they are squeezed from the diffusion layer to the bulk followed by "fresh" liquid. The mass transfer through the interface causes the local change in the interfacial energy which itself generate the movement

at or near the interface. Following, the relationship between the interfacial convection and mass transport have been pro-

posed in the previous paper (2):

$$Bo^* = const. Ste^Z .$$

(3)

Experimental

The industrial casts were performed at ThyssenKrupp Nirosta in Bochum works. The cast steels were Cr-Ni stainless steels AISI 304, 321 and 316Ti with Ti contents of 0.01, 0.3 and 0.3 mass % respectively. The temperature of liquid steel in the mould was approx. 1460°C. Different mould fluxes were used for casting. The composition of the most frequently used flux is listed in Table 1. During industrial continuous casting samples

were taken from the mould as described previously (12). At this sampling method the whole vertical square section including liquid steel, liquid slag, sintered and powder layer is taken in the cc mould in the steel container with 50 mm diameter and quenched immediately in water. After cutting, polishing and preparation of the sample the square section was investigated using LM, SEM and EDS.

Tab. 1 – 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%, CO₂ 5.5-6.8%.

FeO	MnO	P	SiO ₂	Al ₂ O ₃	TiO ₂	CaO	MgO	F	Na ₂ O	K ₂ O	Li ₂ O
1.27	0.04	0.04	33.5	7.05	0.14	38.6	0.81	8.40	8.23	0.50	1.08

Results and discussion

The main components of the investigated fluxes are CaO and SiO₂, which make up together approx. 60% of the mass. The relevant physical properties of fluxes for continuous casting such as viscosity and surface tension are adjusted by adding CaF₂, Na₂O, K₂O, Li₂O and FeO, MnO and MgO. Even small additions and changes in composition can have a considerable effect on these properties. The composition of liquid flux changes during casting because of the reactions with steel at the interface. The change in the chemical composition of the slag from 13 samples taken during casting of AISI 304 is plotted as a bar chart in Figure 1.

Greatest changes show SiO₂ (decreasing) and TiO₂ (increasing). Oxygen is supplied to the liquid metal mainly from (FeO)

and (SiO₂) in the flux, with [Ti], [Mn] and [Cr] in the steel melt being oxidised. Designation () and [] indicates the slag-phase or metal-phase respectively. The greatest exchange takes place between (SiO₂) 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. Δ(TiO₂)/[Ti] during the reaction time (2, 12, 13).

The change of 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 (2, 12, 13).

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

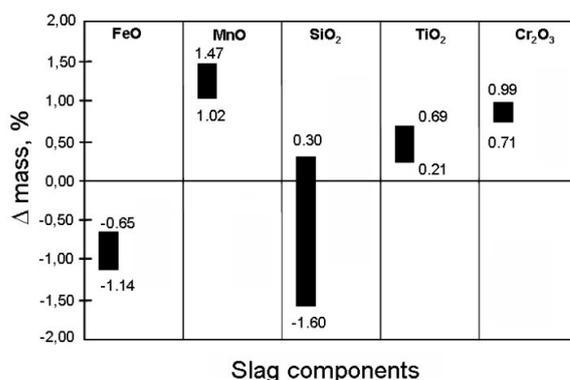


Fig. 1 – Change in the chemical composition of slag during casting of AISI 304 compared to virgin casting powder (C and moisture losses are taken into account).

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In Figure 2 the square section over the whole quenched liquid layer, from liquid metal to sintered layer, is presented. Different solidification structures show clearly the pattern caused by thermal flow. It is generated because the interface to liquid steel is approx. 300 K hotter compared to the upper part with

contact to the sintered layer as reported previously (2). The patterns are visible because of the different solidification structure which is partially glassy and partially crystalline. The length scale of these patterns lies in the range of millimetres.

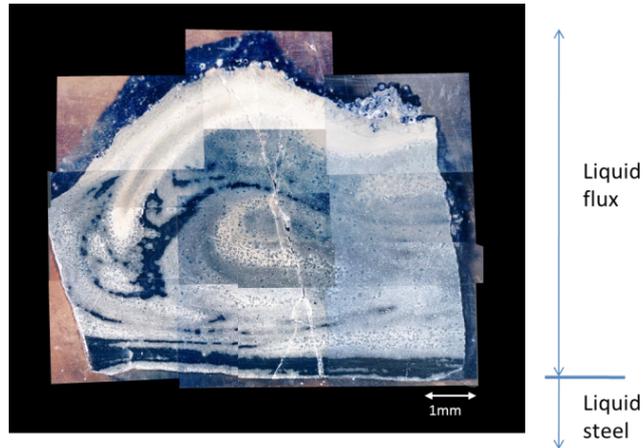


Fig. 2 – Square section over the slag sample taken from the CC mould and quenched in water.

Since [Ti] was present in steel and the change in the (TiO₂) concentration was the highest of all components relative to the content in steel, the effect of the convective flows on the kinetics of the metal-slag reaction was examined on the basis of [Ti] oxidation and absorption into the slag. The effect of interfacial convective flows on the kinetics of the mass transfer with liquid metal was investigated via the ratio $\Delta(\text{TiO}_2) / [\text{Ti}]$ (where Δ represents the difference in the chemical composition of sampled slag and the original powder) as a function of the slag layer thickness (2, 10). The ratio increases continuously with slag layer thickness.

The relationship between the Bo^* and the convection conditions in the slag, as defined by the Steinmetz number Ste containing slag layer thickness as L_c , are examined below on the example of casting steel AISI 304. The experimental results evaluated

in this way are shown in Figure 3. It can be clearly seen that Bo^* increases with increasing Ste . Even with the smallest measured slag layer thickness, Bo^* is greater than 1 (i.e. the total mass transport is greater than the diffusive mass transport). It can be reliably assumed that under the experimental conditions, the interfacial flows always occur as soon as liquid slag is formed. They make a continuous contribution to the total mass transport up to approx. 20 times the mass flux by diffusion (see values of Bo^* in Fig. 3). For values of Ste higher than ca. $5 \cdot 10^3$ (marked with thick stroke), thermal convection occurs and the relation between Bo^* and convective flows has to be described using another function as reported previously (2). In this case the flow conditions are described by the product $\text{Ste} \cdot \text{Ra}$, which takes into account as well the interfacial convection as the thermal one.

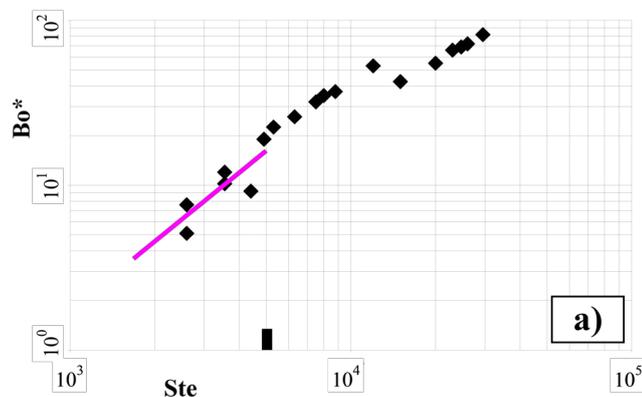


Fig. 3 – Modified Bodenstein-number Bo^* for TiO₂-absorption into the casting flux as a function of Steinmetznumber Ste (valid in the range of Ste up to $5 \cdot 10^3$) for cast steel grade a) AISI 304.

Further investigations of the slag solidification structure show specific structure near to the interface with metal.

The overview is shown in Figure 4. Alternating crystalline and partially glassy layers arranged parallel to the interface with metal are clearly visible. Glassy structure in this sense means not real glass, as can be detected by XRD, but structure with

much less crystals than the other one. The thickness of the layers is 50 to 80 μm , in other samples up to approx. 150 μm . The slag layer thickness on the meniscus of liquid steel was in this case 5 mm. At these conditions no any thermal convection can occur (2).

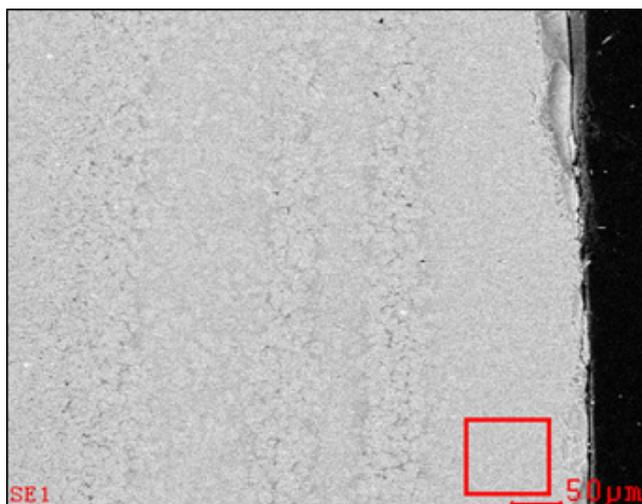


Fig. 4 – Solidification structure near to the metal interface (on the right side).

Detailed inside view to the both kinds of layer are presented in Figure 5 a) and b). In the crystalline structure a big number of metallic droplets exists a) and in the partially glassy structure much less b). During casting Fe, Cr, Mn and Ti in steel are oxidised at the interface and introduced into slag, compare Figure 1. During cooling down of samples (similar situation exists in the gap between strand shell and the mould wall) iron oxide and chromium oxide are reduced by residual carbon (11) producing metal droplets with $<1 \mu\text{m}$ to $2 \mu\text{m}$ in diameter.

They are composed of iron with 2 to 7 mass % chromium. As the reduction process runs before the slag solidifies they act as nuclei for the slag crystallisation. In nearly each crystal a

metallic droplet can be detected in the centre. The quenching of the samples was performed in this way that the steel container with slag and liquid steel was immersed into water with the bottom side.

As the steel has higher thermal conductivity compared to slag, the heat was mainly removed downwards through the liquid and then solidified steel.

Following, the first slag layer adhering to steel cooled with higher rate than the layer above it. This could be the reason for partially glassy solidification. Layer in bigger distance from the interface have higher temperature and during cooling more crystals can be produced, as shown in CCT diagrams

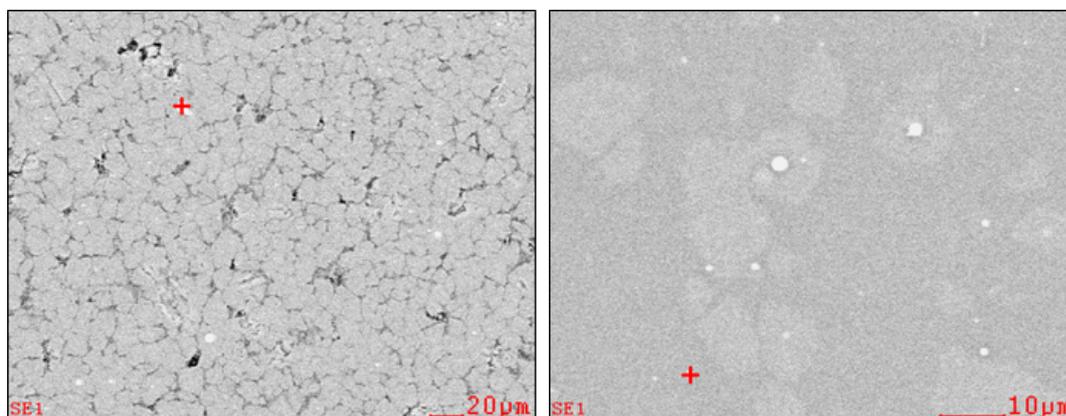


Fig. 5 – Solidification structure in the a) crystalline and b) partially glassy layer; magnification from Fig. 4. White points are metallic droplets.

e.g. in previous investigations (14, 15). The occurrence of layers and their order is difficult to explain if we assume the static state in liquid slag. In Figure 2 was shown that thermal convection in any case exists (even during cooling of the sample) if the slag layer is thicker than 6 mm (2). In the sample shown in Figure 4 with 5mm slag layer thickness thermal convection do not exists. Therefore it is evident that the movement of liquid slag producing small scale vorticities and layering must be caused by interfacial convection. Such phenomena were previously investigated in physical models (16). The different solidification structure is finally the result of local thermal history and probably small differences in the content of at the interface oxidised iron and chromium.

Interfacial convection occurs when gradients of interfacial tension along the interface exist. On the basis of oxygen transfer through the interface investigated in similar samples it was previously concluded that the interfacial tension should be close to zero (17). Other investigations of interfacial tension between liquid slag or flux and steels using the drop weight method show values between 0.6 to 1 Nm⁻¹ (18). However, the values measured with drop weight method correspond to nearly equilibrium state which cannot be assumed in the real continuous casting process. In the last case high mass transfer rates exist because of the specific flux composition, its low viscosity and short contact time between phases. Therefore much lower interfacial tension can be expected. On the other hand the precipitated metal droplets in the slag and clear interface between slag and metal, even if sometimes perturbed, indicate that interfacial tension should have in average a certain value higher than zero. It is not homogeneously distributed at the

interface because of intense mass exchange and because of convection flows with connected renewal of the interface. All these factors lead to local gradients of interfacial tension producing interfacial turbulences.

Conclusions

Samples were taken in the mould during the industrial continuous casting process and quenched in water. The sampling technique enables the investigation of the whole slag layer between the contact to liquid steel and the sintered layer. The investigation of slag samples was focussed to the area near to the interface with liquid steel.

The results can be summarised as follows:

1. Near to the interface with metal a layered structure in the solidified slag was found. In alternating order the layer consist of crystalline and partially glassy structure. The thickness of these layers lies between 50 and 150 μm .
2. In the centre of nearly all crystals metal droplets with $<1 \mu\text{m}$ to $2 \mu\text{m}$ in diameter exist. They are produced by reduction of iron and chromium oxide during cooling of samples and act as nuclei for slag crystallisation.
3. The order of layers and their length scale indicate strongly the existence of interfacial convection in the liquid state.

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LIST OF SYMBOLS

Bo	Bodenstein-number
Bo*	modified Bodenstein-number
D	diffusion
F η	viscous force
F p	inertia force
F σ	surface tension force
L $_c$	Characteristic length
m_i	mass flux density
Ra	Reyleigh-number
Re	Reynolds-number
Sh	Sherwood-number
Ste	Steinmetz-number
We	Weber-number

η	dynamic viscosity
ν	kinematic viscosity
ρ	density
σ	interfacial tension
τ	shear stress
[]	metal phase
()	slag phase

Indices

D	diffusion
Σ	total
i	substance ir

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