THE INTERFACIAL CONVECTION IN TWO IMMISCIBLE FLUIDS AND ITS EFFECT ON MASS TRANSPORT

Piotr Scheller
Freiberg University of Mining and Technology, Germany

ABSTRACT

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 determine the total reaction rate. Looking to the metal-slag reactions the transport of reactants in the given slag phase limits the kinetics. In 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. Some aspects of transport phenomena for the case of thin slag layer reacting with liquid steel will be analysed and the experimental results presented.

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. 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, as a result of chemical reactions at the phase boundary.

The objectives of the present study were to conduct basic investigations in the laboratory into convective flows near the interface using various model fluids. Furthermore were to describe the effect of the interfacial convection on the bulk flow in thin liquid layer using dimension free characteristic number and to describe the mass transport near the interface for high temperature processes in a suitable way allowing the evaluation of experimental results. The description developed is used to evaluate the metallurgical reaction process.

INTRODUCTION

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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 [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, as a result of chemical reactions at the phase boundary [2].

The objectives of the present study were to conduct basic investigations in the laboratory into convective flows near the interface using various model fluids. Furthermore were to describe the effect of the interfacial convection on the bulk flow in thin liquid layer using dimension free characteristic number and to describe the mass transport near the interface for high temperature processes in a suitable way allowing the evaluation of experimental results. The description developed should be applied to evaluate the metallurgical reaction process.

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 slag layer on top of the liquid metal. First, the conditions prevailing when a liquid layer lies on top of another without undergoing mixing are considered. The upper liquid has a free surface exposed to air, Figure 1.

If the interface between two liquids is disturbed locally by the action of, for example, surfactants or high mass transfer densities due to reaction between the phases or diffusion, the interfacial tension, as a rule, decreases and the adjacent liquid films on either side are pulled towards the not disrupted interface.

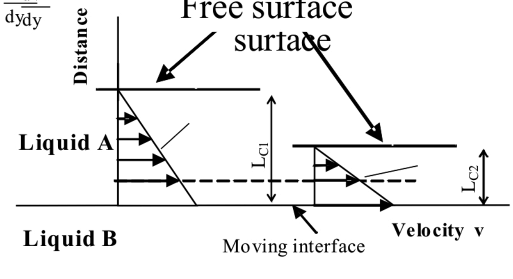

Figure 1: Velocity vectors at different thickness of liquid layer Lc; the velocity at the moving interface is equal in both cases

When mass transfer through the interface occurs the local decrease of the interfacial tension follows. This produces free energy which is converted to the movement energy in the direction of the high interfacial tension, as no new surface or interface will be generated or interface disappear. The calculations of the oxygen mass transfer rate for the mould flux-steel reaction [3] confirm this situation. Moreover the transfer of the metal cations will enforce these instabilities. In areas where the established interfacial film breaks e.g. due to chemical reaction between phases or increase of surfactant concentration, a new interface is formed with a lower interfacial tension. Subsequently, flows and diffusion in both fluids result in the renewal of the layers in the vicinity of the interface causing the interfacial tension to increase again.

To describe the flow caused by the disruption of the inter-facial tension, first consider a very thin (in extreme case monomolecular) interfacial film between the areas of high and low interfacial tension which moves away without friction from the point of disruption. As the initial shear stress τmax (or the difference in interfacial tension $\Delta\sigma$) increases, the distance x from the disruption point will also increase for constant fluid properties. This movement of the near interface layer was observed in experiments using various fluids.

In the following, based on the similarity theory, a functional relationship will be derived between a geometric parameter and the material properties in question. This makes it possible to quantify the flow conditions in the vicinity of the phase boundary and to compare different material systems with each other using dimension free description.

The movement of a briefly accelerated volume element or fluid layer is determined by a given surface 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 Lc, 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:

$$L_c \Delta \sigma \rho \eta^{-2} \equiv \frac{F_\sigma F_\rho}{F_\eta^2} \tag{1}$$

where $L_c\Delta\sigma\rho\eta^{-2}$ is denoted the Steinmetz number *Ste* in honour of Professor Eberhard Steinmetz as derived in the previous paper [4]. 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 tension ($\tau_{max} = \Delta\sigma/\Delta x$ = 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 move 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, grad τ decreases with increasing Ste (because *Ste* ~ 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 interfacial tension.

Mass Transport

With respect to the analysis of the mass transport description discussed in the introduction the modified Bodenstein number Bo* is 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 cased by diffusion $\dot{m}_{i,D}$:

$$Bo^* = \frac{\dot{m}_{i,\Sigma}}{\dot{m}_{i,D}} \tag{2}$$

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 interfacial reaction controls the total rate then Bo* ≤ 1. Otherwise if the reaction products or transferred species are transported away by convection (e.g. thermal convection) then Bo* > 1. If interfacial convection occurs they are squeezed from the diffusion layer to the bulk followed by *fresh* liquid.

The interface convection contributes to mass and heat transport in the liquid layer and influences the kinetics of the reactions between phases. Therefore, for a fluid layer of given thickness and given physical properties, the disturbance of the force balance causes convection flows and has the following effect after the phase boundary reaction has taken place:

$$\Delta\sigma \rightarrow v \rightarrow \dot{m} \rightarrow \Delta C \tag{3}$$

where Equation (3) correspond to interface convection. The driving force Δσ lead, in this case, directly to a change in the chemical composition ΔC in the reacting phase [6]:

$$\Delta C = f(\Delta\sigma) \tag{4}$$

and increase the Bo* number. If other kind of convection exists, e.g. thermal or forced convection as described in previous paper [4], the Bo* number will increase additionally. Following, the relationship between the interfacial convection and mass transport have been proposed in the previous paper [5]:

$$\mathrm{Bo}^* = \mathrm{const.Ste}^{Z} \tag{5}$$

EXPERIMENTAL

Interfacial Flows

In these investigations, different non-miscible fluids were layered above one another. Deionised water was always covered by different fluids with lower densities. The adjustable parameter was the height of the covered layer which was varied within the range of 3 mm to12 mm. The surface tension in the model experiment was varied between 0.0018 and 0.047 Nm^{-1} (liquid metal/flux 54.10^{-3}) and the dynamic viscosity between 10^{-3} and 84.10^{-3} $\mathrm{kgm}^{-1}\mathrm{s}^{-1}$ (0.6-1.2 $\mathrm{kgm}^{-1}\mathrm{s}^{-1}$ for liquid steel/flux).

The local disruption of the interfacial tension in model experiments was induced by injection of a surfactant solution consisting of 23% anionic and 4% amphotere surfactants. Depending on the properties and the height of the upper layer as variable parameter, the dimensionless Steinmetz number *Ste* (Equation 1) varies between 7 and 47 for oil, 172 and 1146 for hexanol and $34{\bullet}10^3$ and $228{\bullet}10^3$ for petroleum.

Mass Transport

For the observation and measurement of the mass transport the similar experimental arrangement as described above was used. As immiscible liquids 1-butanol (density 848 kg/m^3, viscosity 3.324 mPas, surface tension 24.2 mN/m) and water were used and the transfer of Rhodamine 6G as tracer substance from water to butanol was measured. In one case the transport of Rhodamine 6G only by diffusion was measured while in other case its change due to induced interface convection.

In the industrial experiments samples were taken from the mould during the continuous casting process. Mass exchange between mould flux and stainless steels with different Ti content were measured by analysing of quenched mould flux. The chemical composition of steels and mould fluxes are given in previous paper [5].

Measurement Methods

A high speed camera was used to record the movement of a dyed tracer at the interface between the two non-miscible fluids from a top view. Furthermore, the particle image velocimetry (PIV) method was used to investigate the fluid flow in both phases.

The measurement of the Rhodamine 6G transport was performed using the laser induced fluorescence (LIV) method and the same laser after the system was calibrated.

RESULTS AND DISCUSSION

The propagation velocity at the interface observed with high speed camera is given by the measured displacement of the dyed tracer. The measured velocities are plotted over the distance from the surfactant injection position (disruption position) as shown in Figure 2. The results show that with increasing layer thickness the movement velocity increases for constant material properties. Assuming that the total reduction of the interfacial tension $\Delta\sigma$ corresponds with the interfacial tension σ between the both phases the Steinmetz number can be calculated.

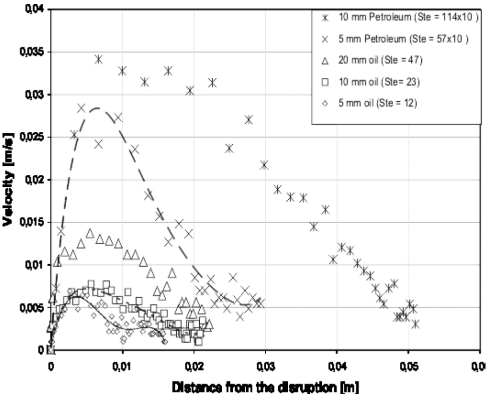

Figure 2: Dependency between the velocity of the tracer and distance from the injection position

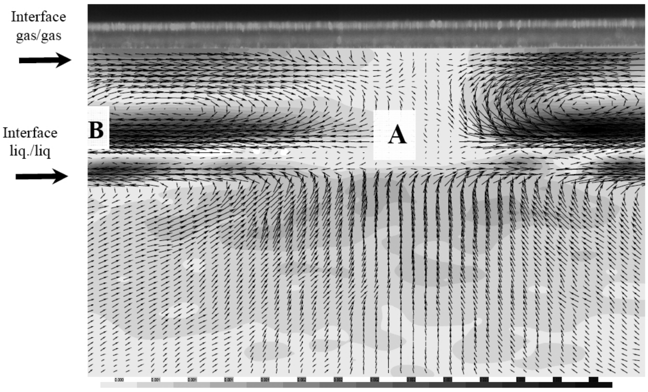

Figure 3: Induced fluid flow by injection of surfactant as vector and grey coloured magnitude map

The velocity of the area nearest to the injection position, in which interface undergoes an acceleration from a static position, increases with liquid layer thickness and following the growing Steinmetz number. After reaching a maximum, it decreases with increasing distance from the injection position.

In Figure 3 the calculated velocity vectors from PIV measurements are depicted above the grey colour coded map according their velocity magnitudes. In this Figure the point A and B are declared as references for further investigations of the spatial velocity distribution and the variation of the velocity depending on time.

It can be deduced that the spatial magnitude of the velocity depends on Steinmetz number. The maximal velocities for the point B (as shown in Figure 3) are depicted over the varied Steinmetz number, as shown in Figure 4. For more accurate observation using the high speed camera a good correlation between the *Ste* number and the velocity near the interface is observed.

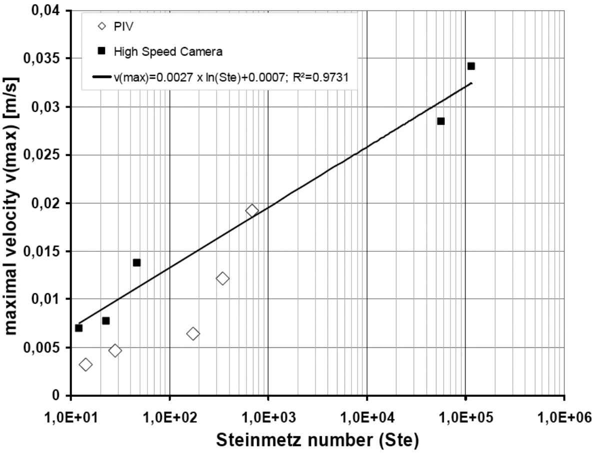

Figure 4: Maximal velocity at the interface as a function of Ste number measured with PIV method and high speed camera

In the continuous casting processes liquid fluxes are in contact with liquid steel. For this case with flux layer thickness above the meniscus of L_c = 5 mm and assuming change of σ

down to zero the Ste values is $2.7 \cdot 10^3$ to $5.4 \cdot 10^3$. Therefore the range of the Ste values of liquid used in present experiments covers also the metallurgical conditions.

The transfer of Rhodamin 6G from the bulk of the aqueous solution through the interface to the bulk of the organic phase butanol was measured in the same experimental arrangement and using the LIF method. The two dimensional area was enlighten by YAG-laser and the fluorescence intensity as a measure for the concentration was recorded with CCD camera (FlowSense M2 8bit). In the first experiment no any convection in both phases existed and the mass transport took place only due to diffusion. In Figure 5 the concentration profiles of Rhodamin 6G are plotted on both sides of the interface and their change with time. It is clearly visible the decrease of the concentration in the water phase and the increase in the butanol. The positive gradients on the butanol side exist due to the higher solubility of Rhodamin 6G compared to water. In the second experiment the same procedure was used. After 1800 s the surfactant was added using the injection needle directly at the interface and the change in the concentration 2 mm from the injecting point was recorded. The concentration change on both sides of the interface is plotted in Figure 6. In the first seconds after the injection the concentration in the upper liquid decreases as the enriched layer is removed and fresh liquid supplied and then strongly increases. The increase is caused by generated torus vortex which transports back the volume elements with high concentration towards the interface. The situation showing the local turbulence near the interface is given in Figure 7.

The flow stagnates with time as the fresh volume elements are transported to the interface and following the interfacial tension increases. In Figure 8 the course of the change of concentration normalized for both experiments to the state at 1800 s (injection of the surfactant) after overlaying the water solution is plotted. The course reflects the interfacial flow and end at higher level compared to the starting position due to higher transferred mass.

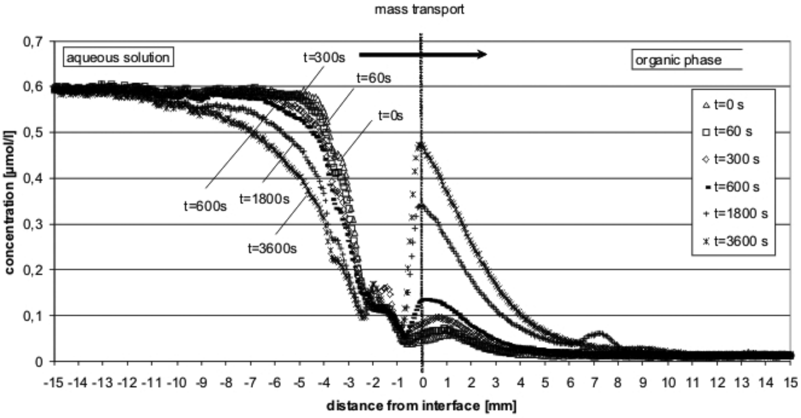

Figure 5: Change in the concentration profiles due to diffusion of Rhodamin 6G from aqueous solution to the organic phase

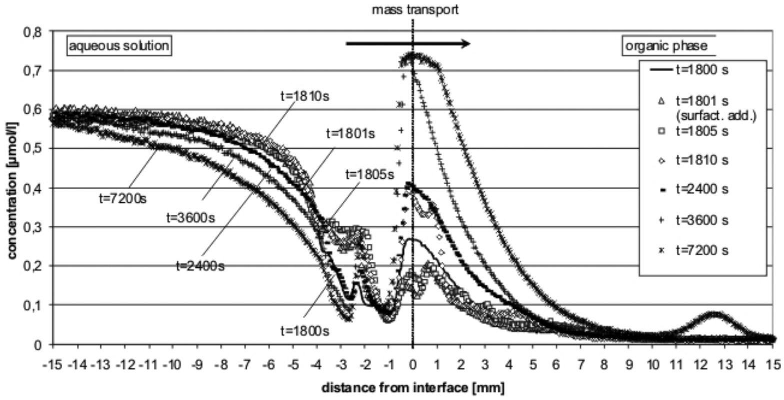

Figure 6: Change in the concentration profiles due to diffusion and transport by interfacial convection of Rhodamin 6G from aqueous solution to the organic phase. Addition of the surfactant at t=1800 s

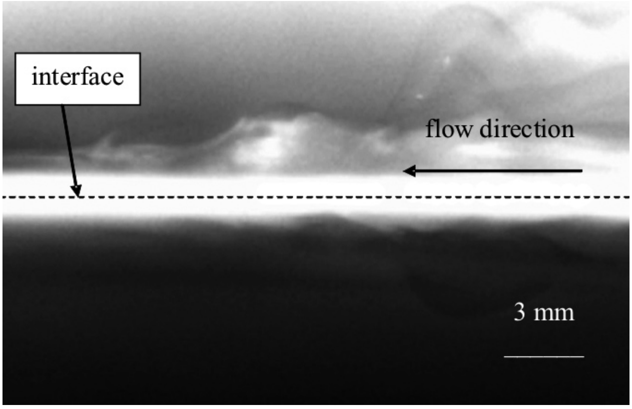

Figure 7: Turbulence near the interface caused by surfactant addition recorded using LIF method

The calculation of mass transport densities in the case of diffusion and in the case of diffusion with only one superimposed movement by interfacial convection shows the increase of the *Bo** number by the factor of 1.1 to 1.5 due to the effect of the interfacial convection. In metallurgical systems much higher interfacial tensions exists which cause more intense interfacial turbulence and consequently lead to higher values of the *Bo** number.

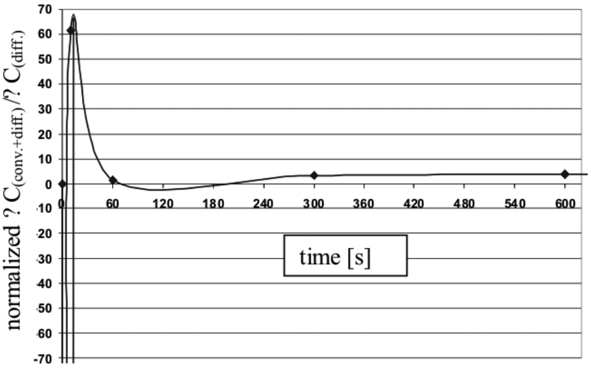

Figure 8: Change of normalized concentration caused by convection and diffusion and only by diffusion

In the casting process considered here, the sources of oxygen are (FeO) and (SiO_2), with [Ti], [Mn] and [Cr] being oxidised (parentheses and square brackets denote slag phase and metal phase respectively). The greatest exchange, in particular with Ti alloyed steel grades, takes place between (SiO_2) and [Ti]. Since [Ti] was present in different concentrations in the alloys examined, and the change in the (TiO_2) concentration was the highest of all components, 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 $\Delta(TiO_2)$ / [Ti] (where here Δ represents the difference in the chemical composition of sampled slag and the original powder) as a function of the slag layer thickness [2, 5]. The ratio increases with slag layer thickness of 5-6 mm. Thereafter, it remains largely constant with increasing slag thickness when free convection takes place [5]. This considerably improves mass transport in the slag layer [5], such that the equilibrium distribution value between slag and metal is achieved shortly after the casting powder melts. Increasing casting powder consumption (from 0.40 to 0.65 to 0.70 $kg \cdot t^{-1}$ in casting steels AISI 304, 321/316Ti and 409/430Ti) results in the $\Delta(TiO_2)$ / [Ti] ratio decreasing. The scatter in the results is mainly related to difficulties in reliably estimating the slag layer thickness and furthermore to the non- uniform effect of phase boundary convection on mass transfer.

The relationship between the *Bo** and the convection conditions in the slag, as defined by the Steinmetz number *Ste*, are examined below. To analyse the problem, a combination of the metal alloy and the slag is considered in each case. This ensures that the mass transfer (and thus the mass transfer coefficient) for each system considered can be assumed to be constant. Therefore, the modified Bodenstein number *Bo**, defined in Equation (2), takes into consideration the effect of the convection conditions for each slag-metal combination in the same way. For the calculation the diffusion coefficients as reported in the literature [6, 7] were used.

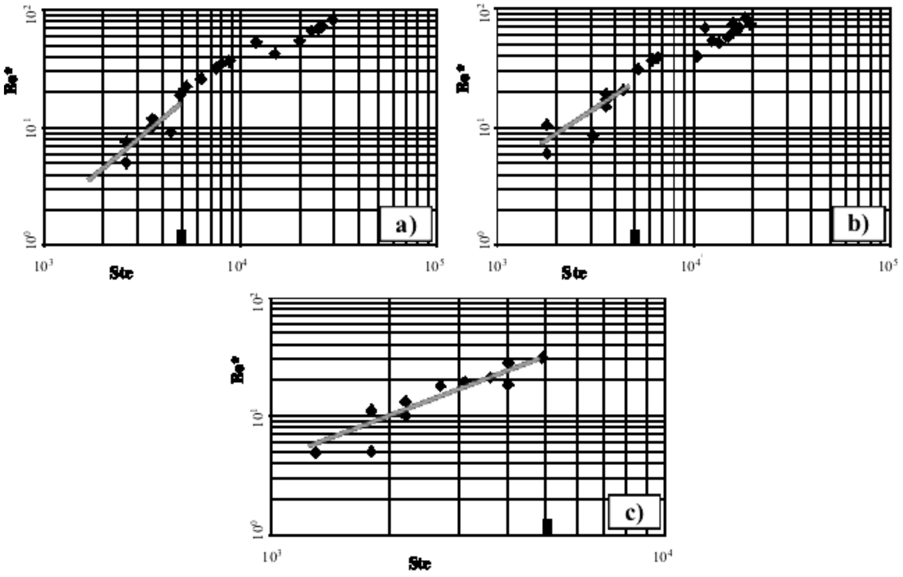

Figure 9: Modified Bodenstein-number Bo* for TiO_2-absoption into the casting flux as a function of Steinmetz-number *Ste* (valid in the range of Ste up to $5 \cdot 10^3$) for cast steel grades a) AISI 304 b) AISI 321 and 316Ti c) AISI 409 and 430Ti.

The experimental results evaluated in this way are shown in Figure 9. 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 basic contribution to the total mass transport up to approx. 20 times the mass flux by diffusion (see values of *Bo** in Figure 9).

The values of the *Ste* number are between $2{\cdot}10^3$ and $5{\cdot}10^3$ and lies within the range of experiments performed at room temperature. Following it can be derived that flow conditions near the interface in the real metallurgical process can be described using the Ste number.

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, 8]. In this case the flow conditions are described by the product Ste·Ra, which takes into account as well the interfacial convection as the thermal one. Experimental results plotted in this range (see Figure 9a-b) show that *Bo** increases with a slightly different slope of 0.23 (related to the value of *Ste·Ra*) compared to that for the results in the range reported here. The value of *Bo** for slags in contact with Cr-Ni steels of the same basic composition, but different Ti contents, differ. With the same Steinmetz number, the *Bo** values are higher when the slag is in contact with Cr-Ni steel alloyed with about 0.3% Ti (AISI 321 and 316Ti) or 0.3%/0.5% Ti (in ferritic steels AISI 409 and 430Ti respectively, with respect to the higher liquidus and casting temperature for these steel grades) than when it is in contact with a steel containing 0.01% Ti (AISI 304). This may be caused by the change in diffusion conditions, or the change in the development of the phase boundary reaction, or the change of the ionic valence which possibly influences the physical properties of the slag (viscosity).

CONCLUSIONS

Flow conditions in thin liquid layer due to disturbance of interfacial tension by contact with lower immiscible liquid have been described theoretically and the results of laboratory experiments are presented. A dimensionless number, $L_c\Delta\sigma\rho\eta^{-2}$ or *Ste* (Steinmetz number), describing convective flows next to the interface in the liquid boundary layer due to disturbance of interfacial tension have been experimentally tested for different combination of fluids. Flow induced by interfacial tension disruption have been investigated experimentally using a high speed camera and particle image velocimetry (PIV). The effect of interfacial flow on mass transport near the interface have been investigated using laser induced fluorescence (LIF) and described by modified Bodenstein number *Bo**. The results can be summarized as follows:

- An abrupt local decrease of interfacial tension induces a toroidal vortices in the thin liquid layer with free surface. In the lower liquid layer a similar recirculation movement of liquid was observed
- The movement velocity of the volume elements near the interface increases with increasing values of Ste as well as the moved liquid volume.
- The dimensionless Ste number is suitable for the description of convective flows caused by the disturbance of interfacial tension.

- The modified Bodenstein number *Bo** describing the quote of mass transport rate density caused by diffusion and convection related to the one caused only by diffusion is suitable for the description of experimental results.
- Interfacial convection always occurs under continuous casting conditions regardless of the thickness of the liquid slag layer and the occurrence of free convection. It contributes to the total mass transport up to approx. 20 times the mass flux by diffusion.

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