Active Tundish Slag

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Abstract: The role of tundish was originally to function as a steel reservoir after the ladle and a distributor into continuous casting moulds. It was designed to obtain proper steel flow pattern through the tundish and to keep thermal losses inside certain limits. When production of “clean” steels with high requirements for oxide inclusions was developed by applying sophisticated secondary steelmaking treatments in the ladle the role of tundish became more critical. It became essential to maintain or even to improve the level of the steel cleanliness by minimizing contamination of steel with air, slag or refractory materials between ladle and the casting moulds.

According to a novel principle of clean steel production the main function of tundish is to maintain the level of cleanliness attained in the ladle by minimizing harmful contamination of steel with air, slag or refractory materials from ladle to moulds. This could be called a “protective or inert tundish practice”. As a consequence, the function of tundish slag is a barrier against reoxidation and thermal losses. By reconstructing tundish to a closed chamber with lid, argon gas shrouding and eventual heating system, tundish slag might be even ignored.

The concept of “active tundish slag” aims definitely at improving of steel cleanliness by “tailoring” a proper tundish slag. In this project active tundish metallurgy was investigated and assessed. Computation of phase diagrams was used as an approach to understand properties and behaviour of tundish slags in casting conditions. Eventual reactions between steel and slag in the tundish were examined by equilibrium calculations. Interfacial phenomena controlling inclusion removal and dissolution into tundish slag were investigated by applying several experimental techniques. Dissolution of alumina and $MgO{\cdot}Al_2O_3$ inclusions into slag were studied by model experiments applying CLSM and DHTT methods. Viscosity of slags was measured by rotating cylinder method at different temperatures. Interfacial tension between steel and slag were measured by drop weight method for several slag/steel systems.

The study showed the complexity and multi-disciplinarity in designing slags which can efficiently absorb macro- and micro-inclusions from different steels and at the same time act as protective cover against reoxidation and thermal losses. The final conclusion was that slag optimization is a challenging issue on which favourable metallurgical and thermal properties should be combined with long-lasting effect during sequential casting operation.

Key words: active tundish slag, inclusion removal, interfacial tension, wetting, inclusion dissolution, reoxidation

1. Introduction

Since the breakthrough of the continuous casting process in the 1960s outstanding progresses have been made in the casting technology i.e. the casting machine itself as well as controlling and optimizing metallurgical phenomena in the casting process. The initial function of tundish was to act as a “reservoir and distributor” for liquid steel from the ladle into the moulds in a multi-strand caster. During the past decades also the great potential of tundish was realized and its functions were extended to improved control of steel temperature and chemistry. As the steel cleanliness has become a main objective for demanding steel grades the role of the tundish is nowadays both to promote inclusion removal from the liquid steel and to prevent appearance of new often macroscopic inclusions, which are most harmful for steel quality. Typically these are reoxidation products formed between the ladle and the mould. As the IISI Study on Clean Steel[1] showed, impressive developments have been done e.g. enlargement of tundish volume for longer retention time, guided flow pattern or argon bubbling to promote inclusion removal and protection of the melt against oxidation from air, slag and refractory materials. Strong interaction between steel and tundish slag has been clearly detected[2]. Recently, endeavours to develop better covering slags for tundishes have been performed and these typically involve a compromise between heat insulation and reoxidation prevention properties and capability to absorb non-metallic inclusions[3-7]. Although promising results were obtained, however, problems still appeared during transient casting conditions and long casting sequences. A growing interest in understanding flow phenomena and inclusions behaviour in liquid steel flow, and reoxidation processes as well as interfacial phenomena controlling inclusion transfer from steel into the slag have strongly encouraged researchers to address the problem again[8-18].

According to another novel principle of clean steel production the function of tundish is not any more to improve steel cleanliness via inclusions removal but rather to maintain the attained level by minimizing harmful contamination of steel with air, slag or refractory materials from ladle to moulds. This could be called a “protective or inert tundish practice”. Accordingly, the function of tundish slag is as a barrier against reoxidation and thermal losses. By reconstructing tundish to a closed chamber with lid, argon gas shrouding and eventual heating system tundish slag might be even ignored[5].

As a contrast to the “inert tundish practice” a concept of “active tundish slag” is here introduced. Overall, the tundish is the last reactor where significant metallurgical operations can still be done. If the steel interaction with the tundish slag can be optimised the steel quality could be maintained and improved in the tundish. An appropriate tundish slag is able to absorb deoxidation and reoxidation products. It can also bind occasional macro-inclusions entering from ladle. Especially in transient casting conditions, start-up and ladle changes in sequential casting, the tundish conditions are most critical and the active slag can show its merits.

Most essential functions of tundish slag are summarised in Table 1 in which also thermodynamic and kinetic constraints and means to influence interaction phenomena are shown. First two topics are examined in this contribution. The first item concerns a typical non-equilibrium condition between steel and slag in the tundish. When the slag contains some unstable oxides they can be reduced by some components dissolved in steel. A common example is a slag containing some “FeO” which should then be reduced by elements like Al, Ti or Si dissolved in the steel. Also other components like MnO and even SiO_2 in slag can be reduced by dissolved aluminium in Al-deoxidised steel. These events are characterised as reoxidation reactions as they cause selective oxidation of components in steel and result in formation of oxide inclusions in steel which can deteriorate cleanliness. These phenomena are studied later in the next chapter.

Table 1. Functions of tundish slag, thermodynamic and kinetic constraints and means to influence.

Function of slag	**Thermodynamics**	**How to influence**	**Kinetics**	**How to influence**
No negative Interaction between Slag and Steel	Low activity of unstable oxides “FeO”, MnO, SiO_2… Compatibility slag/steel	Low contents of unstable components	Avoid strong interaction	Avoid slag emulsification,
Inclusion Absorption Capacity	Liquid, unsaturated slag capable to dissolve e.g. Al_2O_3	Proper slag composition, interfacial properties	Promoting transport of inclusions to steel/slag interface	Flow pattern design and control
Low Refractory Interaction	Chemical compatibility; Basicity	Slag close to saturation with e.g. MgO	Flow pattern on the walls	Calm down Marangoni flow
Protection against Atmosphere	A uniform protecting slag barrier. Inert Ar bubbling	Solid + liquid powder/slag structure	Avoid air contact with steel i.e. eye formation	Avoid too intensive flow
Thermal Insulation	Thermal properties; k, e, Thermal gradient	Solid + liquid powder/slag structure	Gradient across enough thick layer structure	Avoid too intensive flow

Differing from the previous adverse interaction the absorption of inclusions from steel to slag is a positive phenomenon. In ladles it is one principal step in the removal stage of the deoxidation process. In a tundish the phenomenon is still possible but due to transitory movement of the steel it has much less time. Inclusions´ trajectories in the steel flow through the tundish have been calculated and optimal flow patterns have been estimated to transport inclusions close to the steel/slag interface. When arrived near to the interface they have opportunity to move through the interface and dissolve into the slag.

The dissolution phenomenon is extremely important for the final steel cleanliness and, therefore, has been studied quite intensively during the recent years in liquid slags in ladle / tundish / mould conditions, using various techniques: rotating cylinder method[19], rotating disk[20], spear (sampling from the molten slag at a specified time intervals with followed light and electron microscopy) and methods of melting the top of a steel rod together with a slag droplet[21]. A relatively novel technique using the high temperature Confocal Laser Scanning Microscope (CLSM) has as well become available. This technique had been applied to the in-situ observation of dissolution behaviour of inclusions in molten slags[22-29]. The CLSM technique has some advantages compared with the conventional dissolution techniques. First it opens up a continuous in-situ observation of dissolution phenomena. Secondly, the ratio of dissolving species volume to solvent slag volume is very small and comparable with the situation in industrial process vessels, allowing dissolution to take place without a significant change in the bulk composition of the slag. Thirdly, the role of interfacial tension becomes significant in the case of microscopic particles. Differences in interfacial tension between slags and steels with different compositions can have influence on inclusion removal[27]. In this study CLSM technique was applied to observe inclusions dissolution into slag. Also interfacial tensions between selected slag/steel systems were measured.

This contribution had its basic idea in a European joint project. The reviewed results of laboratory experiments were performed at Institute of Iron and Steel Technology, TU Bergakademie Freiberg, Germany. The thermodynamic calculations, examinations and overall discussion were carried out at Aalto University, the Research Group for Metallurgy.

2. Tundish slags´capacity to absorb inclusions

The ability of a tundish slag to absorb inclusions depends on many things concerning physico- chemical properties of the system and the participating phases. Temperature of the through-flowing steel determines the slag temperature at and near the interface, and together with the slag composition the predominance area of liquid slag can be defined. Maximum solubility of ambient inclusions in steel into slag can then be estimated, when mass ratios are calculated too. In the following chapters these aspects are discussed based on selected examples. In the following Table 2 a collection of tundish slags, both commercial products and experimental ones, is listed. Some of them were used in calculations whereas certain slags were used in experiments discussed later. In Table 2 the compositions were reduced to the four main components = 100%. The minor components consisted of Na_2O, K_2O, Fe_2O_3, MnO and TiO_2. Total amount of them was from $\leq 1\%$ up to 5%. Basicity was defined as a wt%-ratio of (%CaO + %MgO) and $\%SiO_2$.

Table 2. Collection of analyses of tundish slags (wt%) in the order of increasing basicity from top to bottom.

Code	Slag Type	CaO	MgO	SiO_2	Al_2O_3	$\frac{\%CaO+\%MgO}{\%SiO_2}$
A0	Al-silicate	5	13	45	37	0.40
A1	Mixed silicate	17	7	44	32	0.55
A2	Mixed silicate	21	13	48	18	0.71
A3	Mixed silicate	22	13	46	19	0.76
A4	Mixed silicate	20	13	42	25	0.79
A5	Mixed silicate	22	13	39	26	0.90
A6	Mixed silicate	22	25	37	16	1.3
B0	Ca-Mg-Al-silicate	32	25	27	16	2.1
B1	Ca-Mg-Al-silicate	45	13	22	20	2.6
B2	Ca-aluminate	51	1	3	45	15
B3	Ca-Mg-aluminate	60	15	5	20	15
B4	Ca-aluminate	48	1		51	≥100
B5	Ca-Mg-aluminate	60	10	10	20	7

2.1 Predominance area of liquid tundish slag

According to the survey of tundish slags performed in the study quite great variety of covering powders or tundish fluxes are used. In some cases it would be better to use the term covering powder as no liquid slag is pursued. As a rule they are outside the scope of this study. As mentioned above the multi-component slag compositions can be simplified to a quaternary system including $\geq 95\%$ of the total. Such a system can be constructed as a quasi-ternary diagram with a constant value of the fourth component. Such slag systems were calculated with FactSage 6.2 programme by using FToxide and FACT databases[31]. Two quasi-ternary diagrams are included here to describe tundish slags. In one case MgO was selected constant = 13wt%. In the other case Al_2O_3 was taken constant = 20wt%. Seven to eight of the slags, can be positioned in the diagrams. It seems that all the acid slags A0-A5 are inside the liquid area 1500°C in both diagrams. In industrial slags minor components like alkaline oxides further expand the liquid area. Basic slags B2 and B4 are almost binary $CaO\text{-}Al_2O_3$ slags with m.p. near at 1400°C. Of quaternary slags B1 comes closest to liquid region and can reach it due to impurities, whereas the other compositions (B0, B3, B5) seem to be solid at 1500°C.

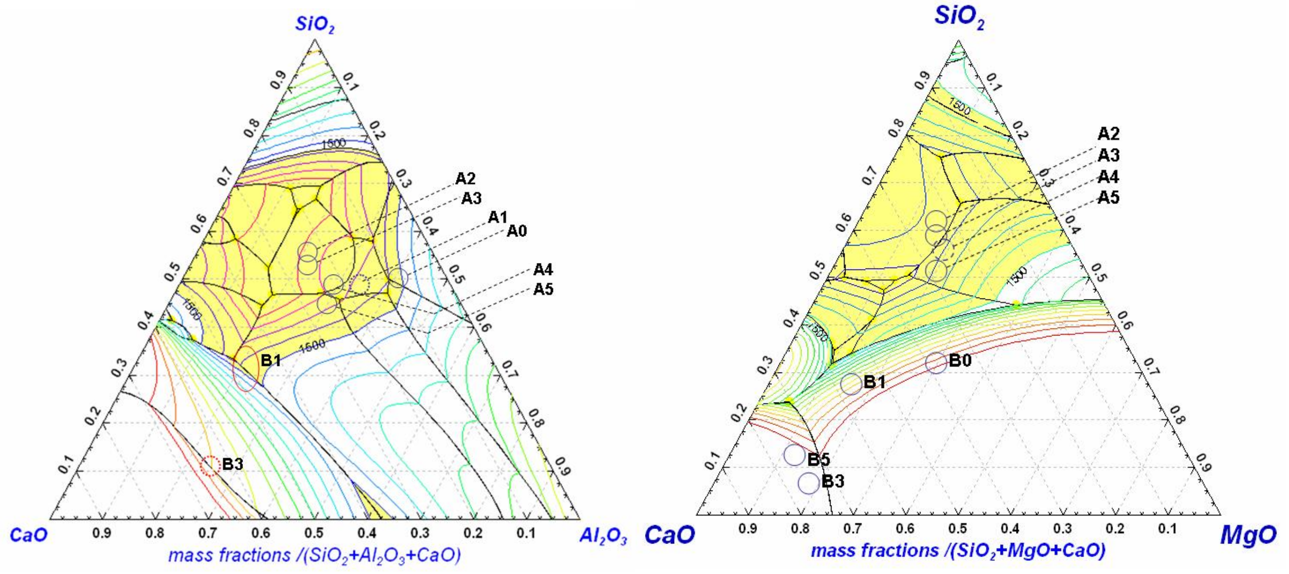


Fig. 1. Phase diagrams with liquidus lines for the system CaO-Al_2O_3-SiO_2 + 13%MgO (left) and for the system CaO-MgO-SiO_2 + 20% Al_2O_3 (right). Liquid area inside isotherm 1500°C is shaded. Slag compositions refer to Table 2.

3. Interaction between steel and slag owing to unstable slag components

Chemical interaction between steel and slag usually means reoxidation: less stable oxides from slag react with deoxidising elements in steel, they are reduced resulting in corresponding metal pick-up from slag and oxide formation in steel. Even small contents of "FeO" are unstable in contact with steel and tend to be reduced e.g.:

$$3(FeO) + 2[Al] = (Al_2O_3)_{inc} + 3Fe \qquad (1)$$

The oxides like Al_2O_3 above are assumed to form in steel melt in the vicinity of the interface. Thus they have possibility to remove to slag but can also remain in steel and appear there as inclusions $(Al_2O_3)_{inc}$. If the content of reactive oxide in the slag is low (few per cents) its influence on steel is minor due to the low slag/steel mass ratio. Hence more important is SiO_2 whose content in tundish powders is typically 20-45%. Then an exchange reaction with steel is most probable:

$$1.5(SiO_2)_{slag} + 2[Al] = (Al_2O_3)_{inc} + 1.5[Si] \qquad (2)$$

As known a_{SiO2} strongly depends on slag basicity. In basic slags it has quite low values ($\leq 10^{-2}$) but increases rapidly when moving over to acid slags. In the following some examples of slag/metal interaction are examined by using data of industrial tundish slags and steel compositions. Tundish slag compositions were presented in Table 2. The steel analyses used in the calculations and/or experiments are listed in Table 3. The steel grade SAE1050 was used in calculations.

Table 3. Steel grades used in calculations and examinations (wt%)

Steel grade	C	Si	Mn	Cr	Al	S	O
SAE1050	0.45	0.18	0.80	0.12	0.015	0.020	0.0015
57Cr3	0.57	0.35	0.90	0.85	-	0.002	0.0020

The concept of the thermodynamic examination of interaction between steel and slag in the tundish starts from the simple principle: in a casting sequence steel from several ladles is passing through the tundish whereas the slag which is formed at the cast start of the first ladle stays almost constant during the whole sequence. In reality, the composition can change due to further flux additions, separation of inclusions from the steel into the slag, lining wear and eventual input of ladle slag at the ladle end. In the following examination a certain fraction of the tundish slag related to the total amount of steel were chosen and was then allowed to react until equilibrium with the steel. The "reactive" slag amount 0.1kg slag/t steel (corresponding to 100ppm) was used in example calculations but also higher amounts up to 0.5kg slag/t steel were tested. Typical amounts of tundish slags in steel plants were in the range 0.3-0.5kg slag per 1 ton steel i.e. a few hundreds of kilograms per one sequence (typically 300-500 t). The equilibrium calculations give a total equilibrium in the steel/slag system. That is of course not a realistic approach in such a transitory system like tundish. But a certain chemical potential difference can be stated between the slag and the by-passing steel which situation results in some exchange reactions happening there all the time. As a consequence the stationary phase, slag will alter toward the equilibrium composition. By thermodynamic calculations it is possible to see the directions of reactions, eventual phases to be formed etc and to make conclusions about prevailing mechanisms. In the underlying figures 0.1kg slag was equilibrated with 1ton steel.

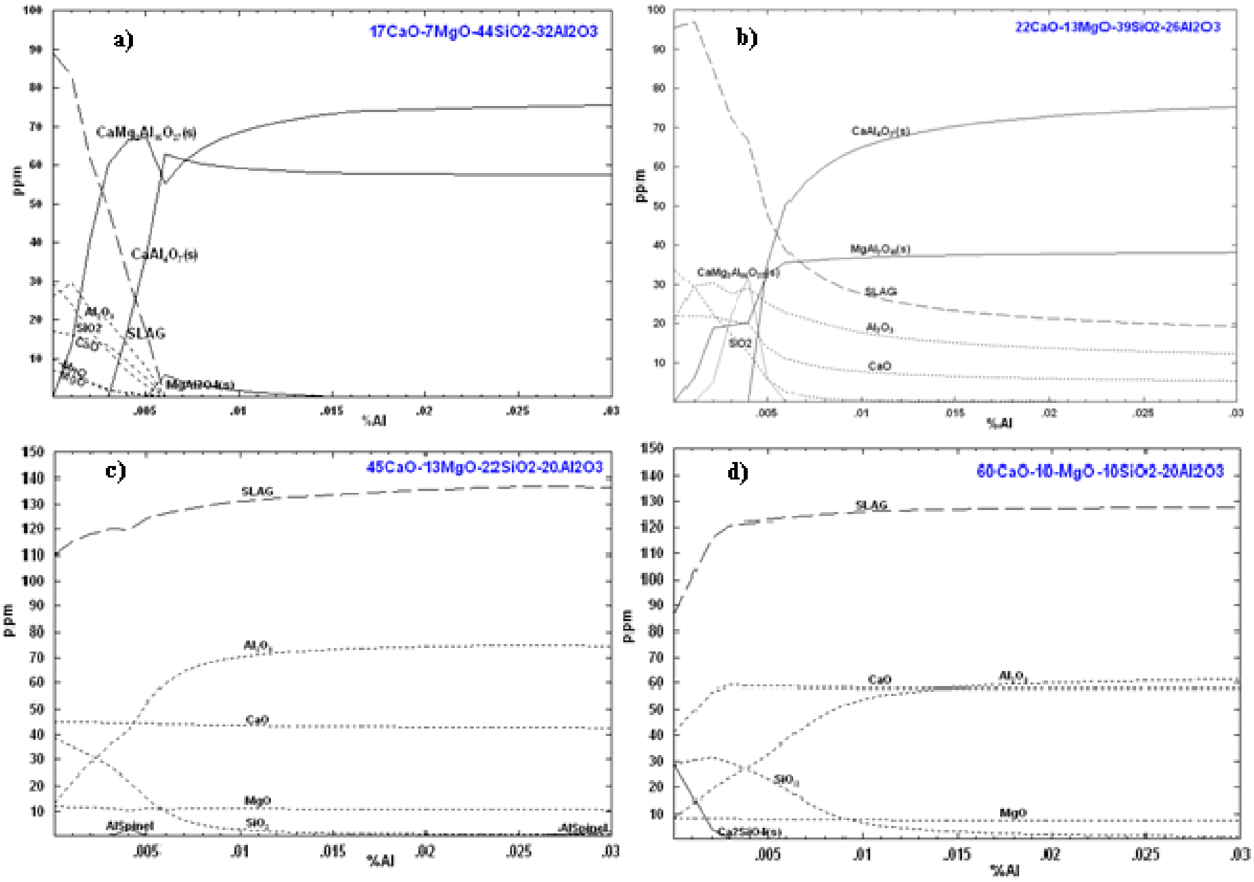


Fig. 2. Various slags equilibrated with SAE1050 steel in ratio 0.1kg slag/1t steel (equal to 100ppm). T =1520°C. a) A1; b) A5; c) B1; d) B5. Components of slag are marked with dotted lines (Al_2O_3, CaO…) and solid compounds with solid lines.

The aluminium content in steel (or actually initial content before the reaction) was used as a parameter as Al is the most reactive dissolved element in steels deoxidized with aluminium. When such a low slag/steel ratio is used like here the steel composition does not change much; some Al is oxidized e.g. in Fig. 2 ΔAl was typically ~ 0.003%. Correspondingly, some oxides are reduced like in the example SiO_2 content was decreased and [Si] is increased. This change is hard to recognize due to relatively high initial Si-content.

As seen in figures the calculations showed that when acid slags (A1 and A5 with basicities 0.55 and 0.90, respectively) react with steel containing aluminium, liquid slag is disappearing and solid Ca- or Ca-Mg-aluminate compounds are formed instead. The phenomenon is strongest with most acid slag A1. On the other hand basic slags (B1 and B5 with basicities 2.6 and 7) can dissolve Al_2O_3 which is formed when SiO_2 from slag is reduced by reaction with [Al]. Only small amounts of solid compounds (Mg-Al-spinel, Ca-silicate) are formed. It can be concluded also that the basic slags in the example have higher capacity to absorb alumina inclusions.

4. Experimental

4.1 Dissolution investigations

Transfers of oxide inclusions from steel to slag and dissolution into slag were simulated by studying dissolution of solid particles (Al_2O_3 and $MgO \cdot Al_2O_3$) into different slags. For particle dissolution investigations the slag was first pre-melted in a platinum crucible and quenched quickly. The premises were a nearly clear glassy slag and a completely filled crucible bottom for the observation of the particle dissolution in Confocal-Laser-Scanning-Microscope (CLSM). In the second step the oxide particle (Al_2O_3 or $MgO \cdot Al_2O_3$) with a diameter of around 300 µm was placed on the top of the glassy slag. The system was then heated to the investigation temperature 1520°C conforming to the operating temperature at steel works. After the melting temperature was reached the slag wetted the particle which sank in the liquid slag down to the crucible bottom. The particle dissolution process was continuously observed with the CLSM equipment, the particle size was measured and normalised over the observation time. Figure 3 shows the dissolution times of alumina and spinel particles in different slags.

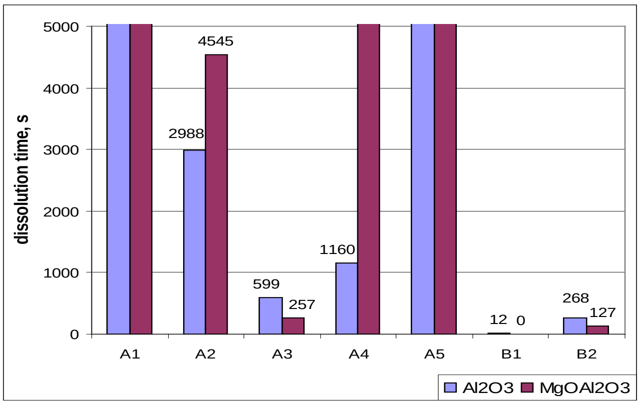


Fig. 3. Dissolution times for different slag/particle systems investigated in CLSM

Both Al_2O_3 and $MgO \cdot Al_2O_3$ particles dissolved quite slowly in slags with low basicity. Only slag A3 behaved exceptionally. The reason is probably that it locates in a eutectic valley in the simplified phase diagram (Fig. 1) whereas slags A1-A2 and A4-A5 have the compositions with higher melting temperatures. Also the equilibrium calculations indicate that some amount of solid phase exists in these slags (comp. Fig. 2). No dissolution of $MgO{\cdot}Al_2O_3$ particle in slag A4 was observed during the investigation time of even 24 min. The slag A4 contains high amount of MgO and Al_2O_3 and with melting temperature of 1520 °C the driving force for spinel dissolution is very small. A shorter dissolution time was measured for alumina dissolution.

The basic slags B1 and B2 contain CaO and Al_2O_3 as main components. The dissolution rates of both kind of particles in these slags were high. The slag B2 is almost binary and has a low melting point which is near the eutectic point of the system. The addition of small amount of alumina leads to decrease the melting point. Slag B1 should have a relatively high melting point due to its composition. The calculations for slag B1 plotted in Fig. 2 show that increase of alumina promotes the formation of liquid slag. Both slags showed a high dissolution rate for $MgO{\cdot}Al_2O_3$ spinel and Al_2O_3 alumina particles. The rapid dissolution of alumina particles into basic Ca-aluminate slags observed here are compatible with the study where solid CaO and Al_2O_3 pieces were pressed together and formation kinetics of liquid Ca-aluminate was measured and detected surprisingly fast in the temperature range around 1500 °C[31].

To obtain intermediate information during the dissolution process, samples were investigated by using Double Hot Thermocouple Technique (DHTT). In the first step a small amount of slag (some milligrams) was pre-melted between two thermocouples, which acted as heating and temperature controlling device in one. After quenching an oxide particle was placed on upper surface of the slag droplet. In the second step the sample was heated up to the desired temperature. After the softening of the slag the particle sank into the bulk and dissolution process started. The evolution of the particle shape was observed by a CCD camera. The dissolution process was interrupted by quenching before the particle was completely dissolved.

After the experiments samples were prepared for metallographic and SEM-investigations. The DHTT samples were embedded, carefully ground and polished until the middle part of the non-dissolved particle was reached. The interface between particle and slag was analyzed with Scanning-Electron-Microscope including energy dispersive X-ray analyser. As examples line scan analyses of interfaces of an Al_2O_3 and a spinel particle with slag A3 are shown in figure 4a and b.

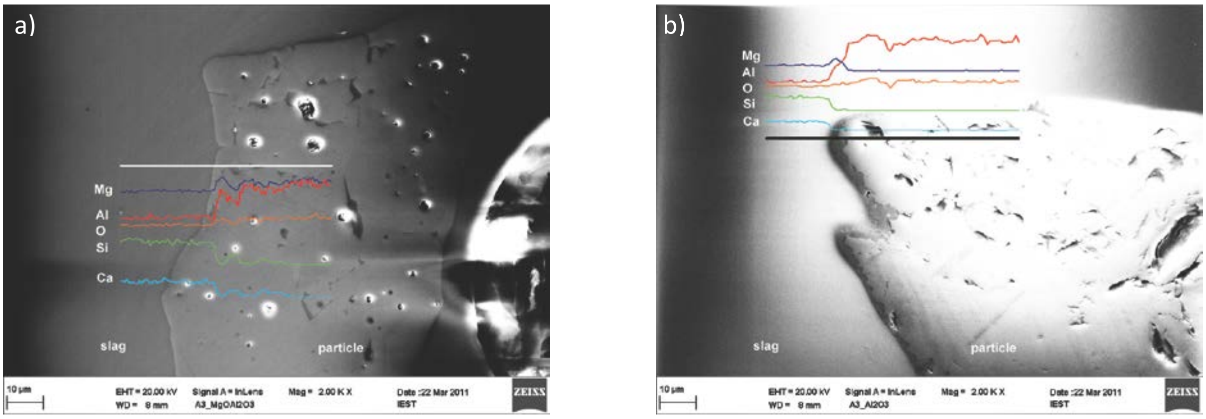
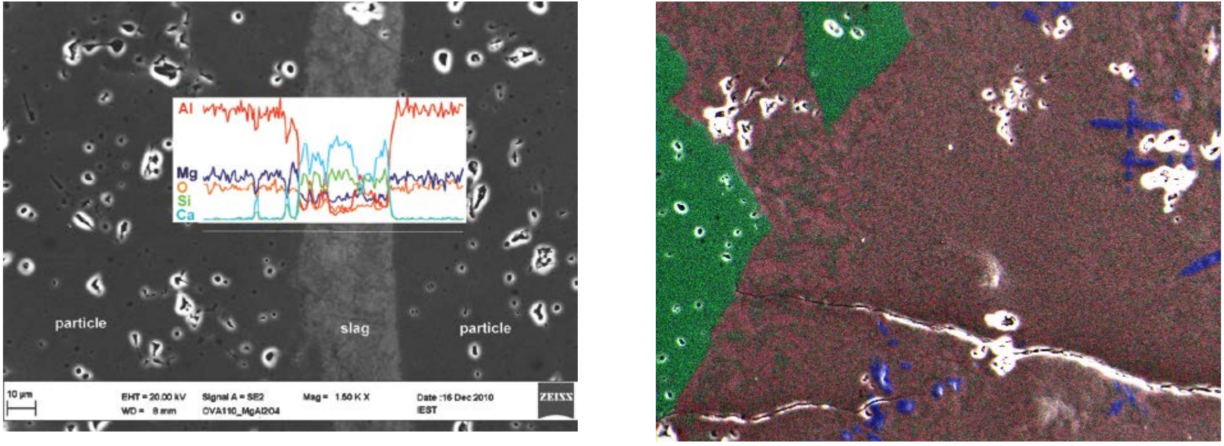


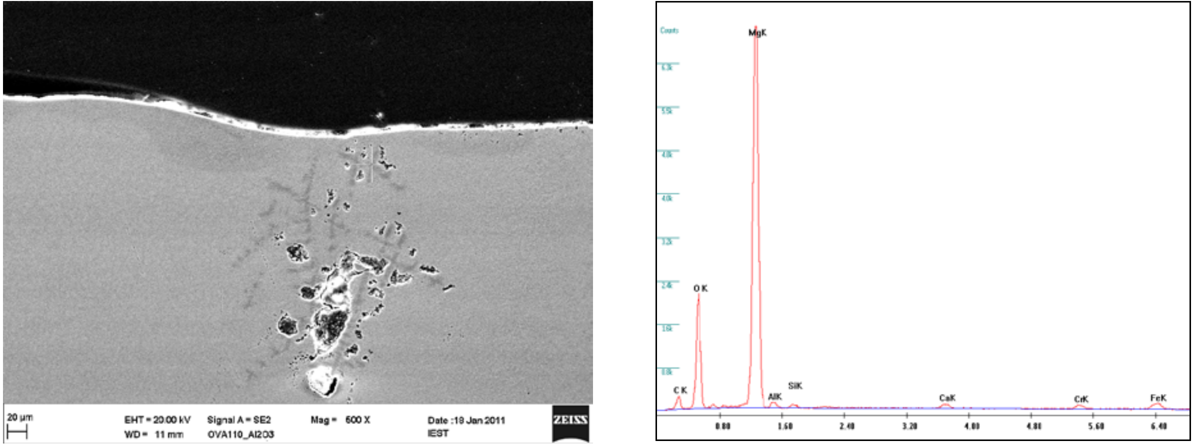
Fig. 4. a) $MgO{\cdot}Al_2O_3$-particle surrounded by slag A3; inside the particle darker areas containing Ca and Si from the slag; b) Slag A3 with Al_2O_3-particle; formation of spinel at the interface of the solid phase

A sharp interface $MgO{\cdot}Al_2O_3$ -particle / slag was observed and therefore no intermediate layer was formed. Inside of the particle areas containing Si and Ca were detected, which can be related to the surrounding slag (see Fig. 4a). The SEM/EDX investigation of the alumina particle in slag A3 shows clearly a boundary layer in the solid phase around the particle (compare Fig. 4b). Using the EDX-analysis of the boundary layer, the ratio of Mg and Al was found to be similar to a spinel structure. Therefore the spinel layer in the solid phase surrounding the particle is formed during dissolution process. Another example is the dissolution of $MgO{\cdot}Al_2O_3$ -particle into slag B1. Figure 5a and b show a line scan and a false colour picture by an EDX-mapping. Dendritic precipitations of MgO in the slag near the solid-liquid interface were detected (see Fig. 5b and 6a). This can be explained by the dissolution of spinel particle and oversaturation of the boundary layer with Mg which finally leads to the precipitation of MgO. This can be supported by heat of solution of solid particles which can produce locally lower temperature promoting the MgO precipitation.


a)

b)

Fig. 5. a) EDX-line scan through a spinel particle infiltrated by slag B1 at the fractured surface; b) false colour picture of the same particle at the interface to the slag (right hand side): red-Ca; green-Al; blue-Mg


a)

b)

Fig. 6. a) SEM picture of Mg-oxide precipitations in the slag B1 during dissolution of $MgO{\cdot}Al_2O_3$ particle b) EDX spectrum of precipitation

4.2 Viscosity of slags

The viscosity of slags was measured in the Couette-arrangement with rotating viscometer. The crashed slag powder was filled in a platinum crucible and heated up in a furnace up to a temperature of 1600 °C. Starting with this temperature the crucible was cooled with 10 K/min while a cylindrical bob rotated inside the slag. Both slags, B1 and B2, show the lowest viscosity at temperature used for particle dissolution investigation (1520°C) followed by the slags 2, A3 and A4 (Fig. 7). Therefore all investigated slags with high dissolution rate for particles (compare Fig. 3) show low viscosity at the experimental temperature. The viscosity seems to be an important kinetic factor for the dissolution process, e.g. via the mass transport by diffusion and convection. The viscosity of the slag B1 increases rapidly with decreasing temperature. This breakpoint indicates the precipitation of solid phase, e.g. MgO, which can be also derived from Fig. 1.

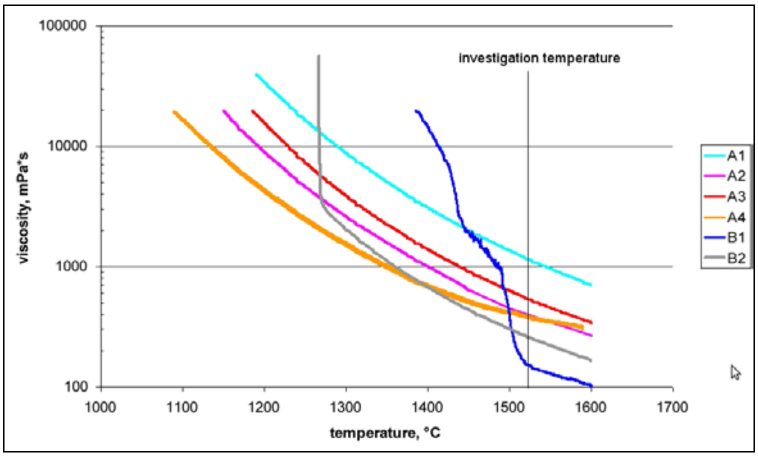


Fig. 7. Temperature-viscosity diagram of investigated slags

4.3 Interfacial tension measurements

The interfacial tension between selected steel/slag systems was determined using the drop weight method[32]. The measurements were performed in the Tammann furnace under argon atmosphere (vol.-%Ar ≥ 99.999). The schematic of the experimental apparatus is shown in Fig. 8.

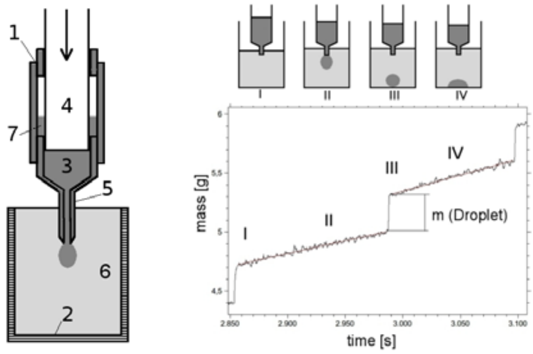


Fig. 8. Schematic of the apparatus used for interfacial tension measurements left: (1) alumina crucible, (2) graphite crucible, (3) liquid metal, (4) alumina piston, (5) capillary tube, (6) liquid slag, (7) copper sealing; Right: mass change vs. time during formation and detachment of a droplet; (I) and (II) droplet growth, (III) mass change due to droplet detachment (IV) formation of the next droplet.

Using a ceramic piston (4) a droplet of liquid metal (3) is formed at the end of a capillary tube (5) which is dipped into liquid slag. The mass m is measured continuously by a high precision balance system. Figure 8 shows a typical mass change during formation and detachment of the metal droplet in liquid slag. Sections (I) and (II) correspond to droplet growth and section (III) corresponds to the weight change due to droplet detachment. Section (IV) is the formation of the next droplet. The mass of the separated droplet correlates directly with the interfacial tension σ between the two liquids, according to Equation 3:

$$\sigma_{\left(\frac{\text{steel}}{\text{slag}}\right)} = \frac{m \cdot g}{2 \cdot \Pi \cdot r \cdot \varphi} \qquad (3)$$

Here *m* is the mass of droplet, *g* is the gravitational acceleration, *r* is the radius of the capillary tube and *φ* the correction factor, which is a function of drop volume and the capillary radius. The correction factor (*φ*) is introduced to compensate for failure, in which case molten metal is not dropped from the capillary tube[33, 34]. The value of correction factor is in the range of 0.6 up to 1.2 and is described by the polynomial equation[35]:

$$\varphi = 1.0069 - 1.2066 \cdot \delta + 1.0096 \cdot \delta^2 \qquad (4)$$

with $\delta = r / V_T^{1/3}$ where *r* is the radius of the capillary and *V* the volume of the droplet.

Measurements of interfacial tension between standard steels and slags were undertaken at 1550 °C. Reactions between steel and slag can lead to either lowered or increased values of interfacial tension. Measurements with drop weight method with certain droplet generation time are consequently influenced by Non-Equilibrium effects. The interfacial tension value estimated for SAE 1050 steel and B1 slag was 960 mN/m and was lower than for the same grade in contact with A1 and A5 slags, ~1050 mN/m and ~1123mN/m, respectively (Fig. 9 left). These are average values based on measurements over 30 minutes. The order of slags is somewhat contradictory when comparing with the slag compositions. Decreasing Al_2O_3 content of 5-10 % should lead to little lower interfacial tension but on the other hand increasing basicity should influence to opposite direction. An eventual interfacial reaction might explain the observation.

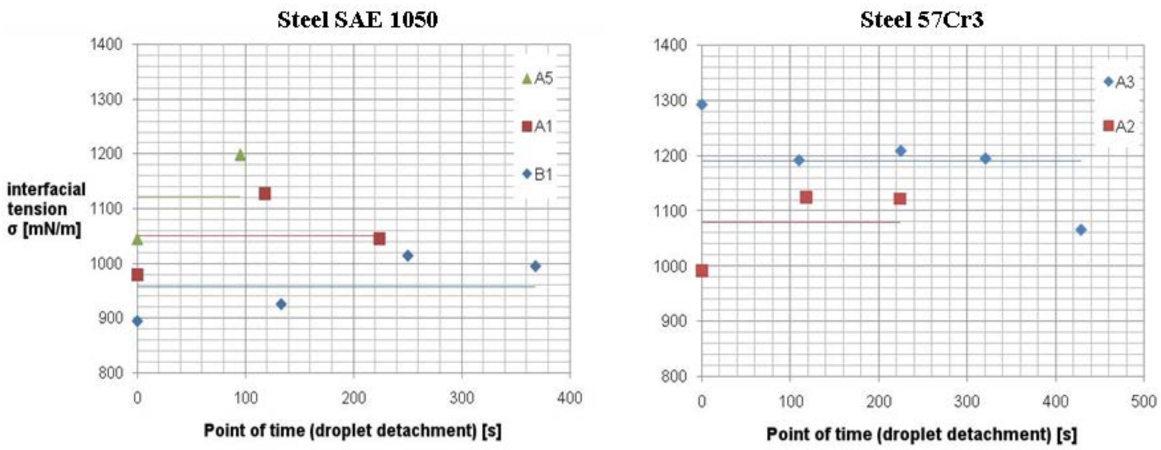


Fig. 9. Interfacial tension values between steels (SAE 1050, 57Cr3) and slags at 1550 °C. Interfacial tension measured during the formation of the first droplet (t=0s) at a volumetric metal flow for droplet formation V = 25–75 $\mu m^{3/}$min.

The interfacial tensions between 57Cr3 steel (Table 3) and two industrial tundish slags at 1550 °C range from ~1075mN/m to 1200mN/m. In the results for the steel 57Cr3 and the slag A2 the high Fe_2O_3 content up to 3.8% have to be taken into account. Fluxes containing highly reducible oxides tend to produce low interfacial tension.

5. Discussion

The basic idea of this study was to introduce the concept of "active tundish slag" which is an essential part of "active tundish metallurgy" practice which additionally includes other phenomena and operations like control of steel flow, temperature, interaction with refractory materials, operations in transient conditions etc. Active tundish slag means maximal utilisation of positive actions in which slag can participate as well as avoiding and minimising negative effects. Most of these phenomena have been intensively studied in various circumstances e.g. in ladle, tundish or mould.

Here we have attempted to make a systematic approach to tundish slags based on the knowledge in literature and our own experiments and examinations. High capacity of slag to absorb inclusions from steel is a key property of an active tundish slag. The deviation from saturation can be used as a measure of absorption capacity. By thorough examination of phase diagrams e.g. by utilising computerised construction of ternary and quaternary diagrams it is possible to compare different slags and to find proper slag compositions with reasonable capacity to dissolve inclusions. A further aspect is the chemical stability of the slag in contact and interaction with the by-flowing steel. Equilibrium calculations showed that the acid slags have a clear tendency to react with Al-deoxidised steel resulting in reduction of SiO_2 from the slag and oxidation of [Al] from the steel forming Al_2O_3 and aluminate or spinel type oxides with magnesia. This phenomenon can thus impair absorption capacity. In this study special attention was paid to dissolution of alumina and MgO-alumina spinel inclusions into industrial tundish slags. Great variability was observed in dissolution rates into different slags. In general, dissolution was much slower in acid slags than in basic slags. Only one of five acid slags was somewhat comparable with the basic slags. Studies on phase diagrams and interaction reactions supported the observations of dissolution kinetics.

Interfacial tension between steel and slag is a factor influencing e.g. inclusion removal from steel to slag and *vice versa* emulsification of slag droplets into steel. It is known that interfacial reaction can collapse the interfacial tension. The measurements done in this work gave expected values between 960 and 1200 mN/m. The results were rather stable although the possibility of interfacial reactions in some systems was not ruled out.

6. Conclusions

The concept of active tundish slag was discussed based on literature survey, computational thermodynamics and experimental investigations. Following conclusions could be drawn.

- Great diversity of tundish powders/slags are used in steel industry differing in chemical and physical properties.
- Acid aluminium silicate type slags are commonly used, but they have potential to react with steel and often have quite limited capacity to dissolve alumina or spinel type inclusions from steel.
- Basic Ca-(Mg-)aluminate type slags have potential for wide use as they can be easily adjusted chemically stable against the steel and to have sufficient capacity to absorb inclusions.

- Sophisticated research techniques (CLSM, DHTT, interfacial tension) give useful information on interfacial reactions and phenomena like inclusions removal and dissolution and slag emulsification.
- Systematic research is still needed to get better knowledge of tundish slag properties and behaviour in casting circumstances and to develop optimal slags for different steel grades and casting conditions.

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References

[1] IISI Study on Clean Steel. State of the Art and Process Technology in Clean Steelmaking. International Iron and Steel Institute, 2004. Editorial Board: Wünnenberg, K., Millman, S., Nadif, M., Marique, C., Sumida, M., Weddige H. ISBN 2-930069-48-1.

[2] V. Manninen, T. Lano, L. Holappa. Low reoxidation tundish metallurgy at Fundia Koverhar steel plant. *Scandinavian Journal of Metallurgy*, 2000, 29(4), p156-165.

[3] R. Boom, J. van der Stel. Thermophysical and Kinetic Consideration for the Selection of a Tundish flux. 76th Steelmaking Conference Proceedings, AIME, Dallas, March 1993, p503-516.

[4] L. Kuchar, L. Holappa. Prevention of Steel Melt Reoxidation by Covering Powders in Tundish. 76th Steelmaking Conference Proceedings, AIME, Dallas, March 1993, p495-502.

[5] Y. Sahai, T. Emi. Tundish Technology for Clean Steel Production. World Scientific Publ. Co, Singapore 2008.

[6] N. Bessho, H. Yamasaki, T. Fujii, T. Nozaki, S. Hiwasa. Removal of inclusion from molten steel in continuous casting tundish. *ISIJ International*, 1992, 32, p157-163.

[7] I-H. Jung, S. Degterov, A.D. Pelton, Y-B. Kang, H-G. Lee. Critical thermodynamic evaluation and optimization of the CaO-MnO-Al_2O_3-SiO_2 system and application to inclusion control. Process metallurgy for ladle-tundish-mould operations., Ladle and Tundish Metallurgy: 41st Annual Conference of Metallurgists of CIM (COM 2002); Montreal, Quebec; Canada; 11-14 Aug. 2002, p131-147.

[8] J. Szekely, G. Trapaga. Mathematical Models of Fluid Flow Phenomena in Tundish Operations. Proceedings of 2nd European Continuous Casting Conference, Düsseldorf, June 1994, p40-45.

[9] L. Zhang, S. Yang, K. Cai, J. Li, X. Wan, B.G. Thomas. Investigation on the Fluid Flow and Steel Cleanliness in the Continuous Casting Strand. *Metallurgical and Materials Transactions B*, 2007, 38B(1), p63-83

[10] L. Zhang. Fluid Flow, Heat Transfer and Inclusion Motion in a Four-Strand Continuous Casting Tundish. *Steel research international.* 2005, 76(11), p784-796.

[11] L. Zhang. Effect of Thermal Buoyancy on Fluid Flow and Inclusion Motion in a Tundish without Flow Control Devices, Part I Fluid Flow. *J.Iron Steel Res Int.*, 2005, 12(4), p20-27; Part II Inclusion Motion. 12(5), 2005, p11-17.

[12] L. Zhang, S. Taniguchi, K. Cai. Fluid Flow and Inclusion Removal in Continuous Casting Tundishes. *Metallurgical and Materials Transactions B*, 31B(2), 2000, p253-266.

[13] R I L. Guthrie, Process metallurgy for ladle-tundish-mould operations. Ladle and Tundish Metallurgy: 41st Annual Conference of Metallurgists of CIM (COM 2002); Montreal, Quebec; Canada; 11-14 Aug. 2002. p3-26.

[14] Y. Wang, S. Sridhar. Reoxidation on the Surface of Molten Low-Carbon Aluminum-Killed steel. *Steel research international*, 2005, 76(5), p355-361.

[15] D-C. Park, I-H. Jung, P.C.H. Rhee, H-G..Lee. Reoxidation of Al-Ti Containing Steels by CaO-Al_2O_3-MgO-SiO_2

Slag. *ISIJ International*, 2004, 44(10), p1669-1678.

[16] K.Y. Lee, J.M. Park, C.W. Park. Rate of reoxidation of ultra-low carbon steel in contact with slag of various compositions. VII International Conference on Molten Slags, Fluxes and Salts. The South African Institute of Mining and Metallurgy, 2004.

[17] K. Beskow, P. Dayal, J. Björkvall, M. Nzotta, S. Du. A new approach for the study of slag-metal interface in steelmaking. *Ironmaking and Steelmaking*, 2006, 33(1), p74-80.

[18] H. Solhed, L. Jonsson, P. Jönsson. A Theoretical and Experimental Study of Continuous-Casting Tundishes Focusing on Slag-Steel Interaction. *Metallurgical and Materials Transactions B*, 2002, 33B(4), p173-185.

[19] S. Taira, K. Nakashima, K. Mori. Kinetic Behavior of Dissolution of Sintered Alumina into CaO-SiO_2-Al_2O_3 Slags. *ISIJ International* 33. 1993(1), p116-123.

[20] X. Yu, R.J. Pomfret, K.S. Coley. Dissolution of Alumina in Mold Fluxes. *Metallurgical and Materials Transactions*, 1997, 28B, p275-279.

[21] W.D. Cho, P. Fan. Diffusional Dissolution of Alumina in Various Steelmaking Slags. *ISIJ Int.*, 2004, 44(2), p229-234.

[22] B.J. Monaghan, L. Chen. Effect of changing slag composition on spinel inclusion dissolution. *Ironmaking and Steelmaking*, 2006, 33(4), p323-330.

[23] B.J. Monaghan, L. Chen, J. Sorbe. Comparative study of oxide inclusion dissolution in CaO–SiO_2–Al_2O_3 slag. *Ironmaking and Steelmaking*, 2005, 32(3), p258-264.

[24] M. Valdez, G..S. Shannon, S. Sridhar. The Ability of Slags to Absorb Solid Oxide Inclusions. *ISIJ International* 2006, 46(3), p450-457.

[25] S. Sridhar, A.W. Cramb. Kinetics of Al_2O_3 Dissolution in CaO-MgO-SiO_2-Al_2O_3 slags: In Situ Observation and Analysis, *Metallurgical and Materials Transactions*, 2000, 31B p406-410.

[26] J.H. Park, I.H. Jung, H-G. Lee. Dissolution Behavior of Al_2O_3 and MgO Inclusions in the CaO–Al_2O_3–SiO_2 Slags: Formation of Ring-like Structure of $MgAl_2O_4$ and Ca_2SiO_4 around MgO Inclusions. *ISIJ International*, 2006, 46 (11), p1626-1634.

[27] S.C. Park, J.H. Park, I-H. Jung, H-G.. Lee. Physico-chemical properties of slags: interfacial tension measurement between liquid iron and slag using synchrotron and dissolution behaviour of Al_2O_3 and MgO in slag. In: Clean Steel, 4-6June 2007, Balatonfüred Hungary, p469-478.

[28] M. Valdez, K. Prapakorn, A.W. Cramb, S. Sridhar. Dissolution of alumina particles in CaO-Al_2O_3-SiO_2-MgO slags. *Ironmaking and Steelmaking*, 2002, 29 (1), p47-52.

[29] K.W. Yi, C. Tse, J.H. Park, M. Valdez, A.W. Cramb, S. Sridhar. Determination of dissolution time of Al_2O_3 and MgO inclusions in synthetic Al_2O_3-CaO-MgO slags. *Scand. J. Metallurgy*, 2003, 32(4), p177-184.

[30] Factsage 6.2 http://www.factsage.com

[31] M. Lind, L. Holappa. Transformation of Alumina Inclusions by Calcium Treatment. *Metallurgical and Materials Transactions B: Process Metallurgy and Materials Processing Science* 41, April 2010, p359-366

[32] J. Campbell: Surface tension measurement by the drop weight technique. *Journal of Physics D: Applied Physics*,1970, 3, p1499-1504.

[33] W.D. Harkins, F.E. Brown: The determination of surface tension (free surface energy), and the weight of falling drops: the surface tension of water and benzene by the capillary height method. *J. Am. Chem. Soc.* 1919, 41(4), 499–525.

[34] M.C. Wilkinson: Extended use of, and comments on, the drop-weight (drop-volume) technique for the determination of surface and interfacial tensions. *Journal of Colloid and Interface Science*, 1972, 40 (1), p14–26.

[35] A. W. Adamson, A. P. Gast: Physical Chemistry of Surfaces, 6th ed., Wiley, New York, 1997, p19-21.