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REVIEW ON INTERACTION BETWEEN SLAG, STEEL AND INCLUSIONS IN SECONDARY STEELMAKING

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The refining function of slags in ladle metallurgy comprises of desulphurization and capture of inclusions, which are removed from the steel melt in the course of deoxidation procedure. In that task, the interaction between the two phases, slag and steel is active and highly beneficial. Further, the slag has a passive, shrouding role when it protects steel from atmospheric oxidation and heat losses. In some cases, slag can even have negative influences as a reoxidation source and eventual origin of harmful inclusions in steel. Conventionally, inclusions in steel are understood as deoxidation products, remained in the steel after the deoxidation process. These, "intrinsic" inclusions are then related to the steel composition i.e. determined by the deoxidizing components in steel, generally Al but even Si, Mn and Ca. However, in intensive ladle treatment the role of the top slag is not only the receiver of inclusions from the steel but pronounced chemical interaction between the liquid slag and metal can take place. Consequently, a component with low activity in the slag e.g. SiO₂ can intensify deoxidation by silicon. By contrast, CaO has a high activity in basic ladle slags and it can interact with steel and bring CaO into inclusions. As a consequence, the type of inclusions can remarkably change. The current paper examines the fundamentals of interaction phenomena between slag, steel and inclusions via thermodynamic calculations, experimental results from steel industry, and observations on related research in the literature.

KEYWORDS: LADLE METALLURGY, AOD, REDUCTION, INCLUSION MODIFICATION, STIRRING,
THERMODYNAMIC CALCULATIONS

INTRODUCTION

Slags are used for refining purposes in primary and secondary steelmaking to collect impurity oxides, to bind impurities (S, P) and to capture deoxidation products i.e. oxide inclusions from the steel melt. Slags have even a protecting role in ladle, tundish and mould when they act as barriers against atmospheric oxidation and heat escape. For these functions, the slags are designed to optimize the positive interaction with steel, and the passive, protecting role between the steel and the environment [1-3]. On the other hand, slags may have negative impacts in ladle metallurgy and casting. Harmful macro inclusions in steel often originate from the slag via reoxidation mechanism of unstable oxides, principally FeO and MnO, or due to emulsified slag particles, directly [4-6].

Great progresses have been achieved in steel cleanliness during the last decades thanks to improved technology and metallurgical knowhow. Developments in ladle metallurgy and casting have made it possible to produce "super clean" steels. In terms of total oxygen content, the acceptable level has reduced from tens of ppm to and below 10 ppm. Of course, the level and criteria for cleanliness are dependent on the steel grade. For many steel grades, 10-20 ppm level is sufficient whereas for demanding bearing steel grades 5ppm O_{tot} has been established [6-8]. Oxygen in liquid steel can be reduced to such low levels by Al-deoxidation. Al₂O₃ inclusions are formed as deoxidation products. A strong intensive treatment in the ladle is necessary to effectively remove Al₂O₃ inclusions and to "clean" the steel. The Al-deoxidation takes place in the steel melt and generally, any side reactions are unwanted. Under strong stirring circumstances, however, a certain interaction of the steel with the covering slag and surrounding refractory lining is inevitable. In these cases, the interaction is harmful. It can impair cleanliness and change the type and characteristics of the inclusion population in the steel. Typical indications of interaction with the slag and/or refractory are the growth of CaO in the inclusions and the appearance of spinel inclusions containing MgO, respectively [9-11].

The advantages of "complex deoxidation" with simultaneous addition of several deoxidizing elements has been well-known e.g. for Si-Mn and Si-Mn-Al deoxidation [12,13]. The same principle of decreased activity of the

reaction product oxide is applicable to the top slag in the reaction zone. This concept of deoxidation with steel/slag interaction is a potential way to intensify deoxidation and to control or “tailor” inclusion type. Such “intensified” deoxidation was applied to silicon deoxidation for steel grades in which deformable inclusions are desirable [14-17]. By using a top slag with low SiO₂ activity and introducing steel into intimate contact with the slag, the deoxidizing power of silicon could be remarkably increased. Another important phenomenon was discovered too. Due to the strong interaction also the inclusion characteristics in the steel was influenced resembling the slag composition. That is very essential especially in steel grades in which soft deformable inclusions are beneficial and hard brittle inclusions (like alumina) are strictly forbidden [17,18]. Certain silicates are such favorable inclusions, and their occurrence in the steel can be secured by a proper slag. In this article, fundamentals of slag-intensified deoxidation and its eventual applications were further examined.

As another example of intensive slag/steel treatment, the reduction stage of AOD process for stainless steel was chosen. It represents a quite different character and magnitude as a reaction system but affords a useful baseline. Thermodynamic calculations were applied to show proper slags for selected steels deoxidized with silicon and the effect of slag on deoxidation efficiency and inclusions were calculated. Comparison with experimental results from steel plants was performed when appropriate. Reaction mechanisms are discussed based on own experimental experiences and observations on related phenomena and processes in the literature. Different techniques for effective utilization of the principle in industrial processes are discussed such as top slag/steel dispersion by gas rinsing, mechanical stirring and injection of slag into steel. Conceivable practices to strengthen beneficial interaction phenomena and to minimize negative ones are discussed too.

INDUSTRIAL PROCEDURES AND RESULTS

Procedures

Two types of carbon steel grades and one stainless steel were selected for the subject of examination. High-carbon (HC) and spring steels were produced in 55 tons BOF and then treated in LF (ladle furnace) for slag-intensified deoxidation. Stainless steel heats 95 tons were made in AOD converter. The nominal compositions of steels and corresponding slags are given in Tab. 1. The influence of slag composition was examined as an example by using three slags with different basicity. Calculations were done with several slag amounts (kg slag/ton steel). Nominal amounts of slags in industrial experiments are printed in bold.

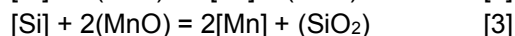
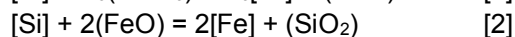
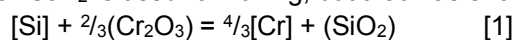
Tab. 1 – Steel and slag compositions in the study.

	Steel composition, wt-%			Slag composition, wt-%						
	C	Si	Mn	Cr	Ni	CaO	SiO ₂	Al ₂ O ₃	MgO	Slag kg/ton
High carbon	0.73	0.22	0.55	-	-	41	34	12	13	8 (5,10)
"	"	"	"	-	-	37.5	37.5	12.5	12.5	8 (5,10)
"	"	"	"	-	-	45	30	12.5	12.5	8 (5,10)
Spring steel	0.55	1.42	0.70	0.67	-	45	35	10	10	8 (5,10)
Stainless	0.03	0.90	1.20	16.7	6.5	58	30	1.5	10.5	100 (50,10)

For High carbon and spring steels the analysis values are after the ladle treatment and for stainless steel after the reduction stage in the AOD converter.

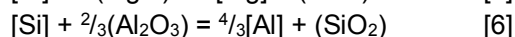
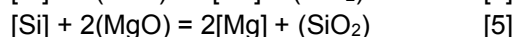
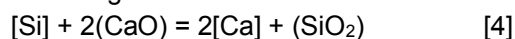
In the case of HC and spring steels, the heats were prepared by “catch-carbon” practice in the converter, which means that the O₂ blow was stopped at an appropriate carbon level under the final specification. Then the steel was tapped into the ladle with concurrent major alloying. Slag stopping was used to prevent BOF slag entering into the ladle. Then the ladle was transported to the ladle treatment station, slag forming agents (lime, doloma, silica) were added to form a proper slag on the ladle. Typical amounts were 6-8 kg slag/ ton steel. The treatment started with strong Ar stirring (5-8 l/min·ton) 10-15 min and turned to soft rinsing (≤ 1 l/ min·ton) for the last 12-15 min. In the AOD process high Cr melt is decarburized by O₂ + inert gas (N₂, Ar) blow to the target carbon content, typically ~0.03% C, whereupon some Cr, approximately 2 percentage points, is oxidized resulting in 25-30% Cr₂O₃ in the slag which then must be reduced back to the steel melt. The slag reduction is normally performed with silicon (in special cases with Al) by adding calculated amounts of FeSi and SiMn into the converter to reduce Cr₂O₃. Furthermore, FeO and MnO are reduced. Additionally, final Si and Mn targets

should be considered. Intensive argon stirring, 650-700 l/min-ton is used for 6 min time, typically. Reduction reactions take place at the bulk slag/steel interface as well as between emulsified liquid droplets in the metal and slag phases. Basic slag with (CaO+MgO)/(SiO₂+Al₂O₃) above 2.0 is beneficial for Cr reduction. Some fluorspar CaF₂ is used for fluxing, but that was excluded from the calculations. The main reactions are:



Square brackets stand for elements dissolved in steel, and normal brackets dissolved in slag, respectively.

When an intensive slag/steel treatment is performed for HC or spring steels, even some reduction of FeO and MnO takes place, but in minor amount as their initial contents in the slag are quite low. As for final inclusion type the following reactions are essential:



There is a thermodynamic driving force for each of these reactions depending on the contents (activities) of these elements in the steel melt and corresponding oxides in the slag.

Interaction between slag, steel and inclusions

Slag/steel interaction can be recognized by verifying the occurrence of reactions [4-6]. The steels in this examination were practically Si-deoxidized and aluminum was only as impurity. Then pick-up of Ca and Mg, and eventually Al from slag to steel could be used as indications of redox reactions i.e. reduction of minor amounts of CaO, MgO and Al₂O₃ into steel. There they can exist as dissolved elements [Ca], [Mg] and [Al], but can also react with present oxide inclusions and thus modify them. In solid samples, Ca and Mg are in compounds and the spectrometric analysis tells the total contents.

In order to concretize the driving force for reactions [4-6] slag/steel equilibrium calculations were performed. FactSage 7.1 software and FSstel database were used [19]. In Tab. 2 analyzed contents of Al, Ca and oxygen are compared with the calculated contents i.e. the steels were equilibrated with slags shown in Tab. 1. Same temperature, 1600°C was used, although in real processes the temperatures for HC and spring steels are somewhat lower and for stainless steels higher (≥1650°C) at the end of reduction stage. Slag amounts in calculations were 8 kg/ton for the HC and spring steels and 10 kg/ton for the stainless steel. The results support the concept of exchange reactions between the slag and the steel since clear pick-up of Ca and Mg were stated. Even Al pick-up is thermodynamically possible, but it is difficult to substantiate, because Si-alloys contain some metallic Al as impurity. Ca and Mg exist in steel mostly as oxide inclusions (at low sulfur level). Considering the average composition of inclusions and the total oxygen content, a certain material balance should be valid.

Tab. 2 – Comparison of analyzed Al, Ca, Mg and O contents in steel and calculated equilibrium contents with slag

	Analysed steel composition after slag treatment, ppm				Calculated equilibrium composition, ppm			
	Al	Ca	Mg	O _[tot]	O _[eq]	Al	Ca	Mg
High carbon steel	<20	1-2	*	20	9	23	1 - 2	4
Spring steel	8-15	1-3	*	20	6	43	1	3
Stainless steel	20-30	10-20	*	30-60	15	80	2-3	11

*Mg is not regularly analyzed, but the contents are comparable with Ca i.e. few ppm in HC and spring steels and somewhat higher in stainless steel.

Inclusions in the first two steels before the treatment with slag are mainly Mn-silicates as very little aluminum and calcium are available in the steel melt. Intensive interaction with slag then brings both Ca, Mg and Al from the slag into inclusions. In AOD converter after the decarburization stage, oxygen activity is very high in the steel melt, the slag is rich in Cr₂O₃, FeO and MnO and inclusions in the steel are influenced by the ambient conditions. When silicon is added for reduction, these oxides are first reduced. Only then the pick-up reactions can proceed.

In Fig. 1 analyzed inclusion compositions were marked in the quasi-ternary CaO-Al₂O₃-SiO₂-10wt-% MgO phase diagrams. Also corresponding range of slag compositions are marked in the Figures. In Fig. 1 (left) it is

seen that inclusions in the example heats in both HC and spring steels were fairly far from the top slag composition. They locate between the isotherms 1400-1500°C. For good deformability of inclusions, the range inside the 1400°C would be recommendable [16-18]. Anyway, the inclusion type has altered from original Mn-silicates (HC) or SiO₂-dominating inclusions (spring steel) to Ca-Al-silicates owing to the influence of the slag. At the same time deoxidation was intensified and remarkably lower dissolved oxygen contents in the steel melt were achieved, which made it possible to attain lower O_{tot} and better cleanliness in the final cast steel, respectively [15].

Example of inclusions and slag composition in stainless steel is in Fig. 1 (right). Before the reduction treatment, the steel melt is highly oxidized, when decarburization has proceeded to low carbon level. The slag is rich in Cr, Fe and Mn oxides, and eventual inclusions in the steel have related compositions. Along the reduction with Si those oxides are mostly reduced from the slag and steel as well and inclusion type is formed via the influence of deoxidizing agents in the steel and the top slag. In Fig. 1 (right), the inclusions marked by square are after reduction and those by diamond a few minutes later after desulfurization. Both types are fairly close to the slag composition.

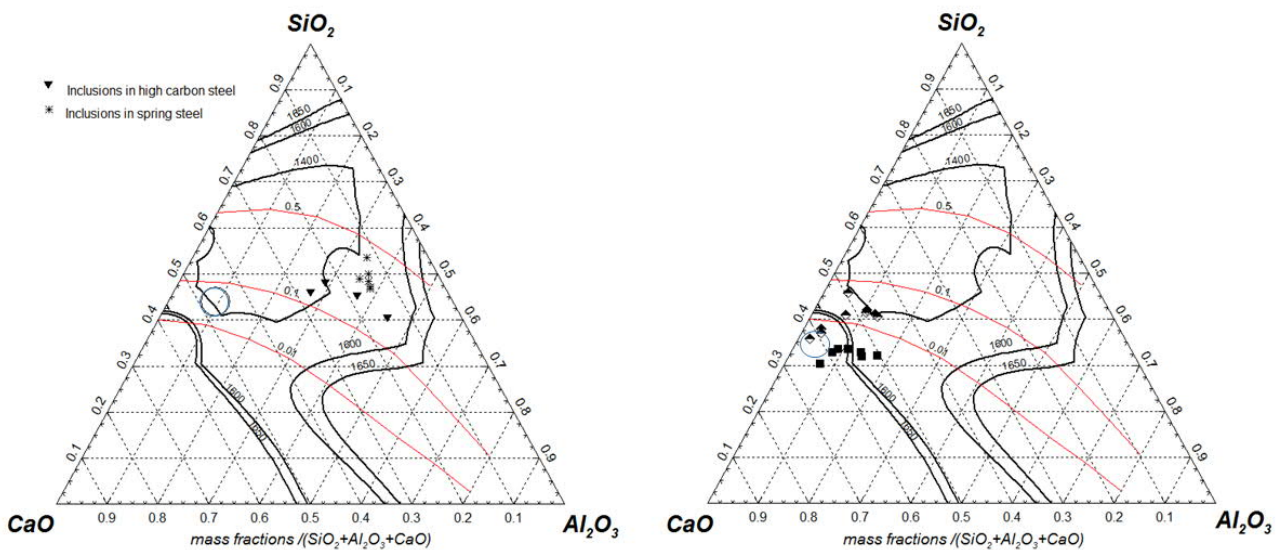


Fig.1 – Analyzed inclusion compositions in HC and spring steels (left) and in stainless steel (right) and comparison with corresponding slags (circles) in CaO-Al₂O₃-SiO₂-10wt-%MgO diagram. Iso-activity curves of SiO₂ also shown.

An example of inclusions in spring steel is in a SEM image in Fig. 2. The element maps and the numerical analysis results correspond to the area of marked inclusions in Fig. 1 left, when the extra components, MgO and MnO are taken into account.

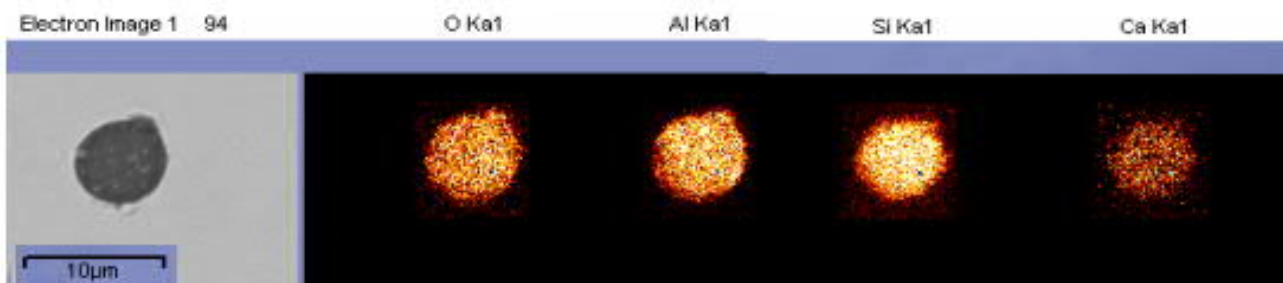
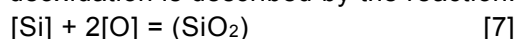


Fig.2 – Example of inclusions in spring steel. Average composition in wt-%: 13CaO-27Al₂O₃- 53SiO₂-2MgO-5MnO.

DISCUSSION

Intensified Si deoxidation

Silicon deoxidation is described by the reaction:



The equilibrium constant is written below, and its value can be found in the literature [20]:

$$K = \frac{a_{\text{SiO}_2}}{a_{\text{Si}} \cdot a_{\text{O}}^2} \quad [8]; \quad \log K = \frac{30110}{T} - 11.40 \quad [9]$$

When the slag is present in the deoxidation reaction, the reaction product SiO_2 can dissolve into the slag, which means that the activity of SiO_2 is decreased remarkably under unity ($a_{\text{SiO}_2} \ll 1$) and then the equilibrium content of dissolved oxygen $[\text{O}]$ should decrease, respectively. This was discussed related to Tab. 2 earlier and in Fig. 3 it is further demonstrated. A basic diagram was first calculated including $[\text{Mn}]-[\text{O}]$, $[\text{Cr}]-[\text{O}]$, $[\text{C}]-[\text{O}]$, $[\text{Si}]-[\text{O}]$ and $[\text{Al}]-[\text{O}]$ deoxidation equilibria in pure iron. Then some $[\text{Si}]-[\text{O}]$ lines were calculated at a specific Si-range for the example steels equilibrated with corresponding slags (Tab. 1). Even the influence of slag amount was tested. Its influence in the cases of HC and spring steels was negligible as the variation range was small (5-8-10 kg/ton steel), but more evident in the case of stainless steel with much larger range of slag amount (10-100 kg/ton steel) as seen in Fig. 3. In the case of HC and spring steels, the dissolved oxygen contents fall down remarkably when equilibrated with slag. Dotted arrows (from square to circle) show the influence of slag. Oxygen probe measurements have confirmed the drop of $a_{[\text{O}]}$. Values 10-13 ppm were measured in spring steel treated with 6 kg/ton similar slag [16].

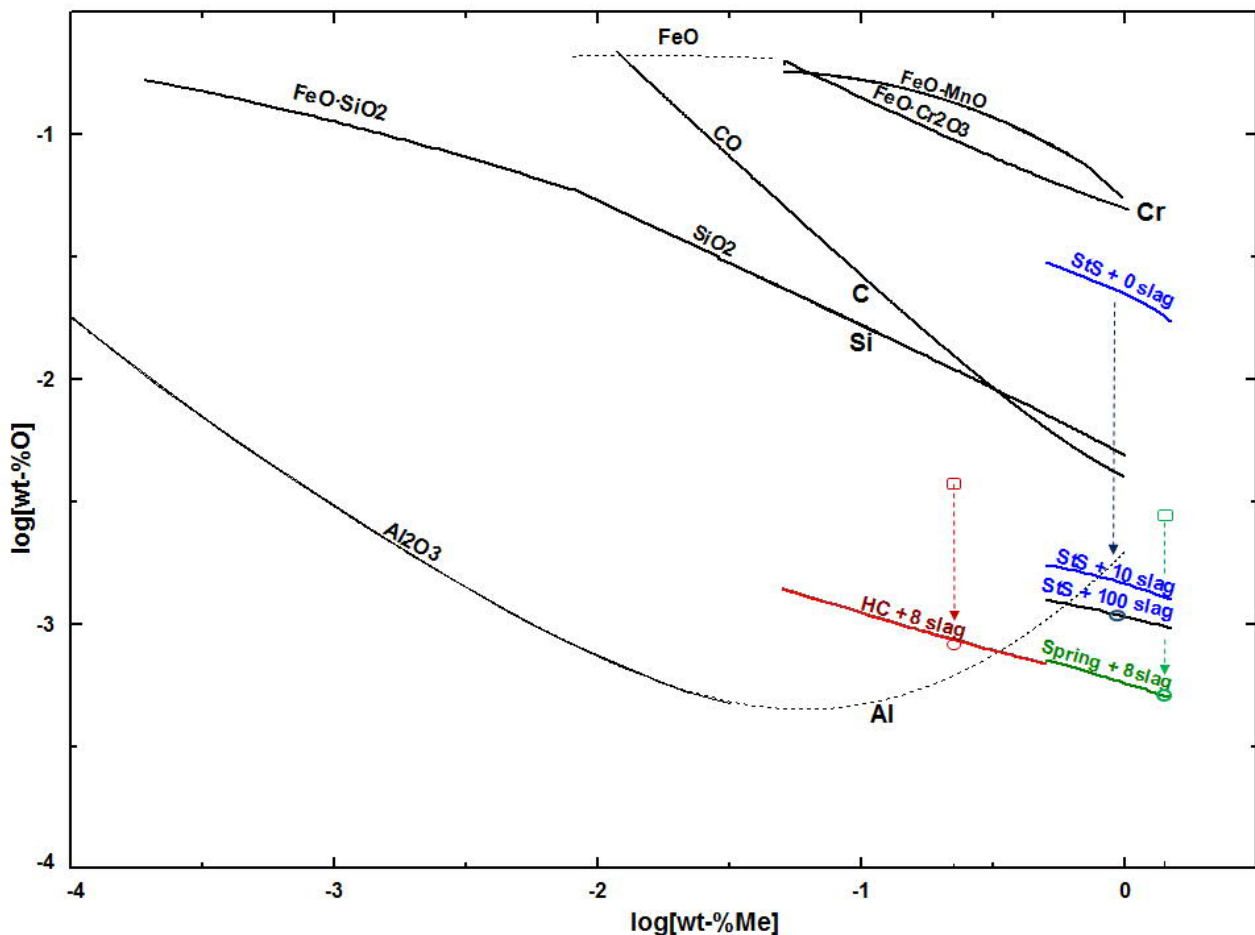


Fig.3 –Deoxidation diagram for $[\text{Me}]-[\text{O}]$ equilibria in pure Fe calculated at 1600°C . Me = Mn, Cr, C, Si, Al. Additionally, $[\text{Si}]-[\text{O}]$ equilibria in example steels with corresponding slags in narrow Si range were calculated (color lines). Dotted arrows indicate the influence of slag at example Si contents. Marking of slag amounts: e.g. 8 slag = 8 kg slag/ton steel.

In stainless steels chromium was observed to decrease the deoxidation power of silicon owing to the negative

interaction (e_{Si}^{Cr} negative) [20, 21]. The line StS + 0 slag in Fig. 3 represents the calculated deoxidation equilibrium in stainless steel without any influence of slag. It is seen that the presence of slag has a strong impact on equilibrium oxygen content, although it remains on a higher level (~15 ppm at 0.9% Si) compared to the lines of HC and spring steels.

Slag reduction

In stainless steelmaking, reduction of slag is a very important stage in the AOD process as it enables high Cr as well as high Mn recovery. Comparison of the final analyzed Cr_2O_3 contents to the initial ones revealed very high (97-98%) reduction degree of chromium.

The thermodynamic calculations, described earlier, give also equilibrium contents of these oxides as well “FeO” in the slag after reduction. These three oxides are here called “reducible” oxides. Calculated values were compared with the analyzed contents in Tab. 3. Although analyzed contents are quite low, they were more than an order of magnitude higher than the calculated ones. This is reasonable as the attainment of total equilibrium between the slag and metal phases (in weight ratio 1:10) is actually implausible. It must be noted also that only a minor part of the “slag” (~5%) is liquid at the example composition (Tab. 1) and the major phases are “ Ca_2SiO_4 ” (~85%) and “MeO” (MgO~10%). This is different from a real industrial slag, into which fluorspar CaF_2 is added as a flux to liquefy the slag. Consequently, the current comparison is only suggestive. In spite of higher analyzed contents, the yield of Cr and Mn is high in the industrial process as adverted above.

Tab. 3 – Comparison of analyzed contents of reducible oxides and calculated equilibrium contents.

Analyzed contents in slag, wt-%			Calculated appr. contents in slag, wt-%		
Cr_2O_3	MnO	FeO	Cr_2O_3	MnO	FeO
0.4-0.7	0.2-0.3	0.4-0.9	~ 0.01	~ 0.015	< 0.01

Mechanisms and modeling of phenomena

Experimental observations raise the question of how these interaction phenomena take place in industrial processes. Two cases, which were discussed here, deviate from each other and thus need separate reasoning. Figure 4 shows schematically slag/steel interaction both in ladle treatment for HC and spring steels and in AOD converter slag reduction for stainless steels. Intensified Si deoxidation and inclusion modification are seen on the left side. Slag composition is designed to have relatively low a_{SiO_2} in the slag. That causes a chemical potential gradient at the steel - slag interface concerning formation of SiO_2 . Thus the Si deoxidation reaction – already stopped inside the bulk steel melt – will go forward at the slag interface (Equation [7]). Similarly, there is a chemical potential gradient at the steel / slag interface concerning CaO and MgO, which can dissolve from slag to steel and together with dissolved [Si] and [O] form complex oxide inclusions with a

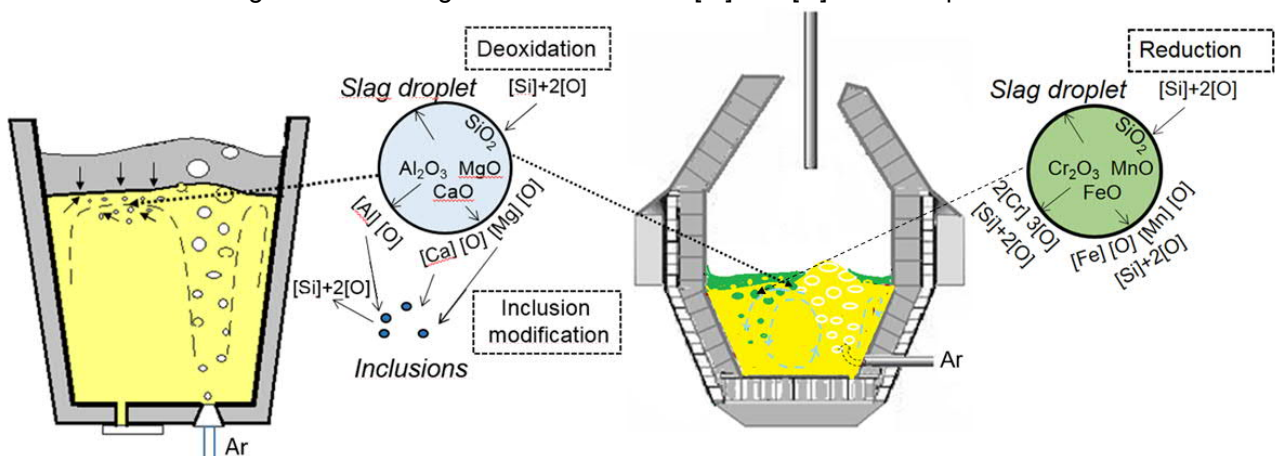


Fig.4 –Schematic presentation on the mechanism of deoxidation and inclusion modification influenced by top slag in ladle (left) and reduction of slag and its interaction with steel in AOD converter (right). Modified from [22, 23].

composition related to ladle slag. Even some Al_2O_3 can be reduced depending on its activity in the slag and content (activity) of dissolved Al in the steel. These reactions are evidently controlled by “surface renewal” and thus dependent on stirring conditions. In ladles, stirring intensity is low in general, and thus these reactions are relatively slow. In practice, it means a partial movement towards equilibria and gradual modification of inclusions closer to the ladle slag composition.

The final type, size and amount of inclusions in solidified steel depend on many factors, both thermodynamic and kinetic constraints. The main event is deoxidation process itself, which is quite complex and continues through all ladle treatments, further in tundish and mold until final solidification. In addition, there is interaction with slag and refractory materials, which can cause reoxidation, and is thus mostly harmful when impairing cleanliness. Then there is the topic of this contribution: interaction between slag, steel and inclusions, which can be harmful, e.g. when producing spinel type inclusions, but can also be beneficial by modifying inclusions to desired composition and properties. All these phenomena influence the final inclusions. It is understandable that the inclusion population is generally not homogenous, but has more or less variation. By strict process control, this variation can be reduced and modeling is a useful tool for this purpose. Comprehensive models to predict inclusions composition in steel are still rather rare. Recently, few articles were published in which the most essential aspects and phenomena were included. Harada et al developed a kinetic model to predict the compositions of steel, slag and inclusions during ladle refining [24-27]. The thermodynamic driving force for each reaction was based on calculated activities of components in phases. The main focus was in formation of $\text{MgO}\cdot\text{Al}_2\text{O}_3$ spinel inclusions. Scheller et al developed a simulation model based on thermodynamic calculations (FactSage) and including kinetic phenomena, deoxidation, dissolution of refractory lining and slag/steel interaction by applying SimuSage package [28, 29]. Spinel formation as well as the effect of Ca addition on inclusions were predicted and compared with industrial results.

Phenomena in the slag reduction stage in an AOD converter are outlined on the right side in Fig. 4. Due to intensive gas rinsing, there is quite powerful stirring. Side blowing of argon through tuyeres generates an eccentric plume, ending up in a dome through the slag in the bubble-bursting region. Reactive slag/steel volume divides into two zones, the minor one against the sidewall on the right in Fig. 4 and the main mixing zone left from the plume. Due to the plume and dome formation as well as high flow velocity in the liquids, remarkable mixing of slag and metal tends to take place via dispersion of liquid phases in each other. Major physical phenomenon concerning the slag/metal interaction is dispersion of slag droplets into the steel. Dispersion of slag into metal phase by gas stirring has been studied quite intensively e.g. [30-32] and with physical and/or mathematical modeling [33-37]. Occurrence of dispersed slag droplets in the steel melt is assumed the main mechanism in slag reduction, whereas the reactions at the bulk steel/slag interface and inside the slag are of minor importance [34, 35]. In the beginning of reduction when silicon (FeSi) is added, its dissolution and transfer to the steel/slag droplet reaction interface is the rate-determining factor. When reduction proceeds and $\text{Cr}_2\text{O}_3/\text{CrO}$ contents decrease in the slag, mass transfer of the reducible oxides in the slag starts to control the reaction rate.

SUMMARY AND CONCLUDING REMARKS

The main object of this article was to highlight the influence of top slag on inclusions in steel. Two examples were examined: (a) moderate argon rinsing in ladle with a selected top slag composition to modify inclusions into deformable silicates in high carbon and spring steels, and (b) slag reduction stage in AOD converter with violent argon blowing and massive exchange reactions between the slag and stainless steel. Following findings were established:

1. It is possible to influence the inclusions in steel and tailor them to desired composition by applying the interaction between the top slag and the steel in argon-stirred ladle. Experimental results in industrial scale have verified that the presence of the slag with low SiO_2 activity can intensify Si-deoxidation. At the same time, minor reduction of CaO and MgO takes place, resulting in dissolved Ca, Mg and O in the steel melt and finally entering inclusions.
2. Computation of deoxidation equilibria in steel and in steel/slag systems and phase diagrams for relevant slags provides the thermodynamic limits of reactions as well how to optimize process conditions. Comparison

of calculations with experimental results tells the reaction degree, e.g. how far the analyzed inclusions were from the calculated equilibrium composition in the ladle treatment example.

3. The aim of slag reduction in AOD converters is to achieve high yield of chromium and manganese from the oxidation period slag into the steel. Industrial experiences have shown that the reduction can take place quite fast due to strong argon side blowing, which brings about efficient rinsing and intensive dispersion of slag droplets into the steel. Dispersed slag droplets seemed to play a decisive role in reduction processes based on results of physical and mathematical modeling. However, a firm experimental verification in industrial AOD process would be most desirable.

4. Slag/steel interaction in ladles is generally applied in desulfurization process, whereas its influence on inclusions has been studied much less. A central problem is that the intensity of gas rinsing is limited in ladles due to the small freeboard. Hence, other techniques like injection of slag powder or mechanical stirring could be potential and should be investigated.

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