

OPTIMISATION OF THE SLAG MODE IN THE LADLE DURING THE STEEL PROCESSING OF SECONDARY METALLURGY

OPTIMIRANJE ŽLINDRE V PONOVCI PRI IZDELAVI JEKLA PO POSTOPKU SEKUNDARNE METALURGIJE

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Prejem rokopisa – received: 2012-10-15; sprejem za objavo – accepted for publication: 2013-03-19

Optimisation of the slag mode in the ladle with the help of briquetted fluxing agents, based on Al_2O_3 under various technological conditions is the object of this paper. The aim of the industrial experiments was to assess the possibility of achieving the optimum chemical composition of the slag that would improve the kinetic conditions of the refining ladle slag during the treatment in secondary metallurgy units. Industrial experiments were focused on comparing the influences of different slag-making agents such as lime (CaO), briquetted fluxing agents and deoxidation agents forming calcium carbide (CaC_2) and granular aluminium (Al_{granul}). During the evaluation of the slag mode in the ladle, samples of the steel from different technological places under operational conditions were taken to assess the desulphurization degree. The samples of the slag for evaluating the chosen parameters, such as basicity, the content of easily reducible oxides, the proportion of CaO/Al_2O_3 and the Mannesmann index, were taken too. Further, the temperature and the oxygen activity in the steel were continuously measured too. The results mentioned in this paper represent the basic information about the possibilities of the slag-mode optimisation in the ladle using different proportions of the slag-making additions, briquetted fluxing agents as well as the deoxidation agents within secondary metallurgy.

Keywords: secondary metallurgy, slag, fluxing agents, steel, desulphurization

Predmet tega članka je optimiranje žlindre v ponovci z briketiranim talilom na osnovi Al_2O_3 v različnih tehnoloških razmerah. Namen preizkusov je bil ugotoviti možnosti za doseganje optimalne kemijske sestave žlindre, ki bi omogočile izboljšanje kinetičnih razmer rafinacijske ponovčne žlindre med postopkom sekundarne metalurgije. Eksperimenti so bili usmerjeni v primerjavo vpliva različnih gradnikov žlindre, kot so apno (CaO), briketirano talilno sredstvo in dezoksidacijsko sredstvo, ki tvori kalcijev karbid (CaC_2), in aluminij v zrnih (Al_{granul}). Za oceno žlindre v ponovci so bili odvzeti vzorci jekla iz različnih mest med postopkom za ugotavljanje stopnje razžvepljanja. Vzeti so bili tudi vzorci žlindre za določanje izbranih parametrov, kot so bazičnost, vsebnost oksidov, ki se jih da lahko reducirati, razmerje CaO/Al_2O_3 in Mannesmannov indeks. Zvezno sta bila merjena tudi temperatura in aktivnost kisika v jeklu. V članku omenjeni rezultati so osnovna informacija o možnostih optimiranja ponovčne žlindre z različnimi deleži dodatkov, ki tvorijo žlindro, briketiranih talil in dezoksidantov pri procesih sekundarne metalurgije.

Ključne besede: sekundarna metalurgija, žlindra, talilno sredstvo, jeklo, razogljčenje

1 INTRODUCTION

The ladle slag presents an important factor influencing the steel cleanliness in secondary metallurgy units. It can accelerate the reactions during a steel treatment between the slag and the metal, such as desulphurization and absorption of non-metallic inclusions. The process of forming ladle slag within secondary metallurgy depends on the quantity of the used slag-making agents (CaO and the fluxing agents based on Al_2O_3), the method of steel deoxidation, the intensity of stirring, the corrosion (wear) of the ladle lining and the quantity of the overflowing slag. A formed mixture of individual oxides represents slag, the composition of which distinctly influences its viscosity, as well as its refining abilities. During a steel treatment the chemical composition of slag is modified with other

additions of slag-making agents, and also by decreasing the contents of easily reducible oxides in order to create a sufficiently basic, liquid slag with a low melting point, contributing to an increase in metallurgical processes. One of the possibilities of fulfilling these requirements within secondary metallurgy is the optimisation of the slag mode in the ladle¹⁻³.

Slag in a ladle is a poly-componential melt whose properties are influenced by the temperature, oxygen activity in slag and in steel, and, above all, by its chemical composition. It was found in literature⁴⁻⁶ that the optimum composition of the slag for the steel deoxidised by aluminium and designated for secondary-metallurgy treatment should have the following oxide proportion: approx. 60 % CaO, 30 % Al_2O_3 , less than 6 % SiO_2 and less than 1 % FeO.

The paper relates to the works of the authors⁷⁻⁹ that focused on using the briquetted fluxing agents (based on Al_2O_3) under plant conditions. The plant experiments aimed at comparing different variants of the proportion of the slag-making agents and deoxidising agents, and at evaluating the achieved optimum chemical composition of the slag, thus enhancing the kinetic conditions of the ladle slag during the treatment in secondary metallurgy units.

2 CHARACTERISTICS OF PLANT EXPERIMENTS AND INDIVIDUAL VARIANTS

Plant experiments for optimising the slag mode were realised during the treatment of steel in the secondary metallurgy units. An evaluation of the influence of the slag-making additions, fluxing agents and the method of deoxidising the steel on the chemical compositions and refining abilities of the slags was made in the following units:

- a homogenization station – HS (blowing of argon),
- a ladle furnace – LF (heated with an electric arc).

Altogether 21 melts were realised under plant conditions, made of unalloyed structural steel S355 in various modifications, the chemical composition of which is given in **Table 1**. It should be mentioned that the plant experiments involved 3 modifications of steel S355, while different maximum contents of sulphur in the steel were required (mass fractions 0.012 % and 0.015 %).

Different variants of the experiments were proposed for creating active slag in the ladle for the treatment in secondary-metallurgy units. These variants differed not only in the used slag-making agents, but also in the

quantity of the additions charged into the ladle. Altogether four variants were proposed, in which the following additions were used: lime (CaO), calcium carbide (CaC_2), granular aluminium ($\text{Al}_{\text{granular}}$) and two types of the fluxing agent, A and B, based on Al_2O_3 . **Table 2** gives the basic characteristics of individual variants.

It follows from **Table 2** that two fluxing agents based on Al_2O_3 were chosen for the plant experiments for all the proposed variants. These fluxing agents contain the same basic components, but they differ in the contents of Al_2O_3 , CaO and in the type of the used bonding agent. **Table 3** gives their basic chemical compositions. Moreover, calcium carbide (CaC_2) was added in order to reduce the contents of easily reducible oxides in the case of a penetration of the furnace slag by the BOF. Granular aluminium ($\text{Al}_{\text{granular}}$) was used for ensuing deep deoxidation; this deoxidation agent was also added in order to reduce the influence of alloying additions and the transition of the formed oxides into the slag in the ladle. The last item is represented by two different doses of lime (CaO) that served as the basic component for the ladle slag.

During the treatment of the steel in the secondary-metallurgy units (HS and LF), the samples of the steel and slag were taken at the following technological places: in the ladle after tapping them from the basic oxygen furnace (BOF) and after their arrival to the homogenization station (sample HS_{start}), before their departure from the homogenization station to the ladle furnace (sample HS_{end}), at the beginning of the treatment in the ladle furnace (sample LF_{start}) and at the end of treatment in the ladle furnace (sample LF_{end}). In the case

Table 1: Basic chemical composition of steel S355 in mass fractions, w/%

Tabela 1: Osnovna kemijska sestava jekla S355 v masnih deležih, w/%

Grade	Range	Chemical composition (w/%)					
		C	Mn	Si	P	S	Al
S355	Min.	xxx	xxx	xxx	xxx	xxx	0.010
	Max.	0.22	1.60	0.55	0.035	0.035	0.060

Table 2: Characteristics of individual variants of industrial experiments

Tabela 2: Značilnosti posameznih variant industrijskih preskusov

Variant of experiment	Additions of slag-making agents (kg)				
	Fluxing agent A	Fluxing agent B	CaC_2	$\text{Al}_{\text{granular}}$	CaO
A	400	xxx	xxx	150	1200
B	xxx	300	100	150	1200
C	400	xxx	100	300	1200
D	xxx	300	100	200	1500

Table 3: Basic parameters of the used fluxing agents in mass fractions, w/%

Tabela 3: Osnovni parametri uporabljenih talil v masnih deležih, w/%

Type of fluxing agent	Chemical composition (w/%)					Used binder	Strength (MPa)
	Al_2O_3	CaO	MgO	Fe_2O_3	SiO_2		
Fluxing agent A	55	15	4	1.5	2	organic	8 – 15
Fluxing agent B	65	11	6	xxx	3.5	sodium silicate	8 – 15

of taking the samples of steel, an analysis of sulphur contents was made, while the analysis of the slag samples was focused on the basic types of oxides and the slag.

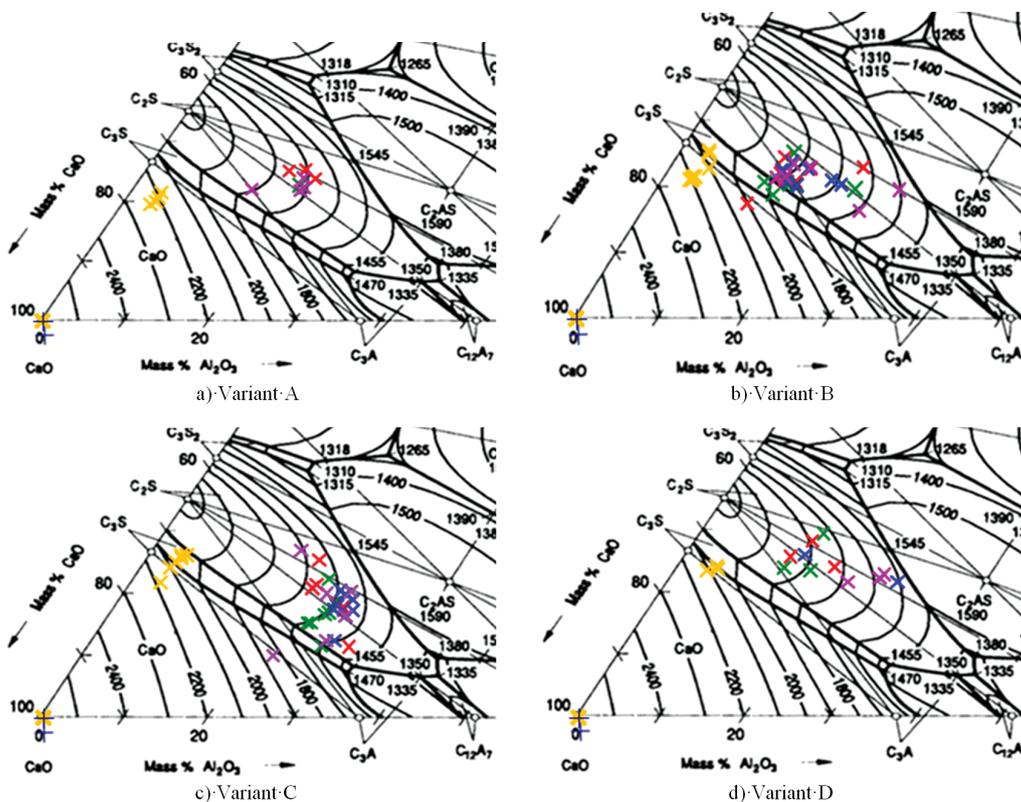
3 RESULTS DISCUSSION

An assessment of the influence of individual variants of the slag-making agents and deoxidation agents on the chemical compositions of the slags was realised in several stages. The first assessment dealt with the evolution of the chemical-composition changes in the ladle slags on the basis of analysing the samples that were taken during the treatment in two secondary-metallurgy units (HS and LF). The obtained results of the chemical-composition changes for individual variants were processed using ternary diagrams presented in **Figures 1a** to **1d**^{10,11}.

It follows from the ternary diagrams for CaO-Al₂O₃-SiO₂ that, in the case of variant A (**Figure 1a**), the temperatures of the slag melting in the ladle vary during the whole treatment in the area above 1800 °C. This may be explained with the low contents of Al₂O₃, approx. 15 % of the slag, with the simultaneously increased contents of SiO₂ in the range from 18 % to 20 %, and with the content of CaO of approx. 49 %. It may be

assumed that the remelt loss of FeSi or FeSiMn, used during the tapping as an alloying addition, might have contributed to the increased contents of SiO₂. Furthermore, it follows from the ternary diagram that, in the course of the treatment, the chemical composition gets slightly modified and the ladle slags approach the boundary area of the melting temperature of 1600 °C. This phenomenon may be explained with the addition of aluminium (Al_{granular}) to the ladle furnace, when the content of easily reducible oxides was reduced.

In variant B (**Figure 1b**) a more distinct evolution of the chemical-composition changes in the slags is visible, but in this case the temperature of the melting slag also varies in the area above 1800 °C. This change may be explained with the low contents of Al₂O₃ in the slag, approx. 13 %, while the contents of SiO₂ were lower than in the previous variant, approx. 17 %, and the contents of CaO varied within the interval from 51 % to 54 %. In this case it may be stated that a lower addition of fluxing agent B had a negative impact on the quantity of Al₂O₃ in the slag, although this fluxing agent contains higher contents of Al₂O₃. However, in the case of several heats, the area of the melting temperature was achieved in the range from 1600 °C up to 1800 °C, namely, in the slags exiting the ladle furnace. This phenomenon may be explained with the additions of lime (CaO), fluxing agent



Note: yellow – BOF slag (sample LD_{end}), red – slag from the homogenization station (sample HS_{start}), green – slag from the homogenization station (sample HS_{end}), blue – slag from the ladle furnace (sample LF_{start}), violet – slag from the ladle furnace (sample LF_{end})

Figure 1: Parts of the ternary diagram for the CaO-Al₂O₃-SiO₂ composition of the ladle slag^{10,11}

Slika 1: Deli ternarnega diagrama CaO-Al₂O₃-SiO₂ sestav žilindre iz ponove^{10,11}

B and aluminium (Al_{granular}), resulting in a modification of the chemical composition of the slag.

In the case of variant C (**Figure 1c**) it may be stated that the chemical composition of the slags varies, from the beginning, in the area of the melting temperatures from 1600 °C to 1800 °C. For this variant the following contents of the basic oxides were achieved: approx. 21 % of Al_2O_3 , approx. 15 % of SiO_2 and between 45 % and 50 % of CaO. In this case a positive influence of the bigger additions of fluxing agent A was clearly confirmed, as well as of a double quantity of aluminium (Al_{granular}) ensuring deep deoxidation. Certain heats move, however, at the boundary of the melting temperature from 1400 °C to 1800 °C. This may be explained with a gradual dissolution of individual components of the ladle slag, and also with the additions of lime (CaO), fluxing agent A and aluminium (Al_{granular}) to the ladle furnace, with the aim of modifying the chemical composition and creating a refining slag.

The biggest change in the chemical composition of the slags during the treatment is shown for the last variant – D (**Figure 1d**). The main part of individual components varies; however, it does so in the area of the melting temperatures above 1800 °C. This may be explained with the low contents of Al_2O_3 , approx. 13 %, and with the simultaneously increased content of SiO_2 , approx. 21 %, while CaO varies within the range from approx. 46 % up to 52 %. In this case it may be stated that the lower contents of Al_2O_3 in the slag actually represent a lower addition of fluxing agent B, added during the tapping. It may also be assumed that the remelt loss of FeSi, used during the tapping as an alloying element, as well as a possible lower addition of aluminium (Al_{granular}) during the tapping, contributed to the increased content of SiO_2 . It also follows from the ternary diagram that several slags exiting the ladle furnace reach a low level of the melting point, 1600 °C. This phenomenon may be explained with the additions of fluxing agent B and of aluminium (Al_{granular}), added to the ladle furnace in order to increase the content of Al_2O_3 in the slag and to reduce the contents of easily reducible oxides.

Apart from an evaluation of the chemical composition of the slags with the ternary diagrams, an eva-

luation of the achieved degrees of desulphurisation (η_s), the values of oxygen activity in the steel ($a_{[O]}$) and the basic parameters of the slags was also made. **Table 4** gives the results for the investigated parameters of the degrees of desulphurisation representing the degrees of desulphurisation for individual technological operations, which took place during the treatment of the steel.

It is evident from **Table 4** that the degrees of desulphurisation had different values for different variants. The total degree of desulphurisation ($\eta_s \Sigma$) varied within the range from approx. 49 % to 57 % (**Table 4**). This is related to the lower initial contents of sulphur in the metal, ranging from approx. 0.025 % up to 0.036 %, and to the required sulphur contents in the steel, ranging from 0.012 % and 0.015 %. It is appropriate to point out that the plant experiments were run in the heats that were not designated for a treatment in a vacuum station (RH) and that their working temperatures varied within the interval from 1572 °C up to 1582 °C.

Variant C (**Table 4**) achieves the best results for continuous desulphurisation. It may be assumed that, in this variant, a gradual dissolution of the slag-making agents takes place during individual technological operations, accompanied by a formation of a liquid refining slag, successfully participating in the steel desulphurisation (45 % to 50 % of CaO, approx. 21 % of Al_2O_3 and approx. 15 % of SiO_2). This trend is confirmed also with the results from the ternary diagram, representing the temperatures of the melting slag (**Figure 1c**.)

The oxygen activity in the steel ($a_{[O]}$) that is an important thermodynamic parameter influencing the steel desulphurisation is the next monitored parameter. The values achieved for individual variants are listed in **Table 5**. It follows from these results that, at the beginning of the steel treatment in the homogenization station (HS_{start}), the oxygen activity varies between 8×10^{-6} to approx. 10×10^{-6} . A decrease in the oxygen activity occurs due to the subsequent treatment in the homogenization station (HS) and the ladle furnace (LF) ranging from approx. 2.5×10^{-6} to 3.0×10^{-6} , as determined in the ladle furnace at the end of the treatment (LF_{end}). This decrease is different for individual variants and the difference in the oxygen-activity decrease is caused by different quantities of deoxidation agents including

Table 4: Degree of desulphurisation during the treatment of steel in secondary metallurgy

Tabela 4: Stopnja razžvepljanja med obdelavo jekla s postopkom sekundarne metalurgije

Variant of experiment	Degree of desulphurisation during the treatment of steel (%)				
	η_s LD	η_s HS	η_s LADLE	η_s LF	$\eta_s \Sigma$
A	27.54	xxx	xxx	16.58	56.72
B	13.79	5.53	18.57	26.65	50.97
C	17.07	12.09	15.99	29.91	55.97
D	11.57	4.63	4.91	37.15	49.47

Note: η_s – degree of desulphurisation: $\eta_s = [S_{\text{start}}] - [S_{\text{end}}] / [S_{\text{start}}] \cdot 100$, η_s LD – degree of desulphurisation during the tapping from the LD converter, η_s HS – degree of desulphurisation in the homogenization station, η_s LADLE – degree of desulphurisation in the ladle during the transport between HS and LF, η_s LF – degree of desulphurisation in the ladle furnace, $\eta_s \Sigma$ – overall degree of desulphurisation

calcium carbide (CaC_2) and granular aluminium ($\text{Al}_{\text{granular}}$).

The best results for the continuous decrease in the oxygen activity were achieved for variant C (Table 5). In this variant, an increased addition of granular aluminium ($\text{Al}_{\text{granular}}$) was positive, ensuring deep deoxidation of the steel. Apart from this deoxidation agent, calcium carbide (CaC_2) was also used, dissolving gradually and supporting the next decrease in the oxygen activity and easily reducible oxides during the steel treatment in the homogenization station ($\text{HS}_{\text{start}} - \text{HS}_{\text{end}}$) and the transport of the ladle with steel to the ladle furnace (LF_{start}).

Table 5: Monitored parameter of steel – oxygen activity in steel

Tabela 5: Prikaz parametrov aktivnosti kisika v jeklu

Variant of experiment	Oxygen activity in steel – a_{O}/ppm			
	HS_{start}	HS_{end}	LF_{start}	LF_{end}
A	xxx	3.50	xxx	2.75
B	8.38	6.75	6.13	2.67
C	10.29	4.14	3.14	2.86
D	10.33	9.00	6.33	2.67

Apart from the degree of desulphurisation and oxygen activity, an evaluation of the investigated parameters of the slags was also made. The results are presented in Table 6 showing the basicity, the content of easily reducible oxides, the proportion of $\text{CaO}/\text{Al}_2\text{O}_3$ and the Mannesmann index.

It is clear from the comparison of individual basicity values B1 (Table 6) that variants A and D may be included into the group of medium basicity, and variants B and C belong to the group of strongly basic slags. The achieved values are related to the contents of CaO and SiO_2 . The resulting degrees of desulphurisation

($\eta_s \Sigma$) for individual variants cannot be, however, substantiated only on the grounds of basicity. This is why an evaluation of the other parameters was also started.

The content of easily reducible oxides was investigated for the ladle slags (Table 6). In this case significantly higher contents were determined for variants B, C and D. These higher contents prove that the furnace slag penetrated into the ladle at the end of the tapping. An addition of calcium carbide (CaC_2) to variants B, C and D was manifested with a gradual reduction of these oxides during its dissolution. This process was supported in the ladle furnace by the additions of aluminium ($\text{Al}_{\text{granular}}$). It may be presumed that a certain quantity of easily reducible oxides is created due to a partial deoxidation and the alloying of the steel.

In the case of the calcium-aluminous proportion it is evident that all the variants (Table 6) achieve the values exceeding the optimum for this parameter (approx. 2.0 to 2.5). Variant C achieves the most stable values, as this parameter varies within the range of approx. 2.1 to 2.5. In the case of variant A, this proportion varies within the range of approx. 3.1 to 3.4, which is caused by the low contents of Al_2O_3 in the slag, approx. 15 %. At the beginning of the experiment, variants B and D achieved the values >4 , which is again confirmed with the low contents of Al_2O_3 in the slag, approx. 12 %. Later, the values for these variants decrease during the treatment, which is caused by the gradual dissolution of fluxing agent B and aluminium additions ($\text{Al}_{\text{granular}}$), while only variant D approached the optimum value.

The last investigated parameter was the Mannesmann index (Table 6), the optimum value of which varies within the range from 0.15 to 0.30. It follows from the

Table 6: Investigated parameters of the slags during the secondary-metallurgy treatment of steel

Tabela 6: Preiskovani parametri v žlindri med obdelavo jekla s postopki sekundarne metalurgije

Variant of experiment	Place of taking the sample	Basic parameters of the ladle slags			
		B1	ERO	C/A	MM
A	HS_{start}	2.30	2.91	3.15	0.15
	HS_{end}	2.56	4.72	3.07	0.17
	LF_{start}	xxx	xxx	xxx	xxx
	LF_{end}	2.64	1.32	3.45	0.18
B	HS_{start}	2.97	8.77	4.51	0.26
	HS_{end}	3.09	5.56	4.41	0.25
	LF_{start}	2.89	4.44	4.0	0.22
	LF_{end}	2.93	1.75	3.73	0.21
C	HS_{start}	3.14	9.62	2.38	0.16
	HS_{end}	3.68	3.39	2.40	0.18
	LF_{start}	3.23	2.42	2.13	0.14
	LF_{end}	3.70	2.17	2.47	0.18
D	HS_{start}	2.29	14.27	4.25	0.21
	HS_{end}	2.39	7.01	4.40	0.20
	LF_{start}	2.34	5.70	3.20	0.15
	LF_{end}	2.44	1.85	2.37	0.12

Note: B1 – basicity: $\text{B1} = (\text{CaO})/(\text{SiO}_2)$, ERO – content of easily reducible oxides: $\text{ERO} = (\text{FeO}) + (\text{Fe}_2\text{O}_3) + (\text{MnO}) + (\text{Cr}_2\text{O}_3) + (\text{V}_2\text{O}_5) + (\text{P}_2\text{O}_5)$, C/A – proportion: $\text{C/A} = (\text{CaO})/(\text{Al}_2\text{O}_3)$, MM – Mannesmann index: $\text{MM} = ((\text{CaO})/(\text{SiO}_2))/(\text{Al}_2\text{O}_3)$

results that in variants A and C, it slightly increases, which is caused by the gradual dissolution of fluxing agent A and aluminium additions ($Al_{granular}$) used to reduce the easily reducible oxides, accompanied by the formation of Al_2O_3 in the slag. The achieved values vary in the range from approx. 0.15 to 0.18, corresponding to the lower degrees of desulphurisation of 57 % and 56 %. However, in the remaining variants, B and D, the values decrease in the course of treatment, which is caused by the increasing contents of Al_2O_3 in the slag. This increase is caused by important additions of fluxing agent B containing Al_2O_3 and aluminium ($Al_{granular}$), used to reduce the easily reducible oxides. As a result of this increase, the values of the MM index decrease, which is manifested by the achieved degrees of desulphurisation, 51 % and 49 %.

4 CONCLUSIONS

Experiments were made under plant conditions to obtain relevant information about the behaviour and influence of fluxing agents A and B, as well as the additions of calcium carbide (CaC_2) and aluminium ($Al_{granular}$) on the chemical compositions of the ladle slags. It is possible to draw the following conclusions from the obtained results:

- it follows from the ternary diagrams for $CaO-Al_2O_3-SiO_2$ that variant C approached the optimum composition of the slag according to the findings from the literature, in which the following contents were achieved: 45 % to 50 % of CaO , approx. 21 % of Al_2O_3 and approx. 15 % of SiO_2 ;
- the lowest areas of the melting temperatures of the ladle slags were achieved with variant C, namely, within the range from 1600 °C to 1800 °C, while some heats varied around the boundary of the melting temperature of 1400 °C;
- it follows from the results for desulphurisation degree that variant C approached the optimum formation of the liquid refining slag, participating in desulphurisation during individual technological operations;
- it follows from the achieved values for the oxygen activity that a higher quantity of deoxidation agents was positively reflected in the lower values of the oxygen activity in the beginning phases of the steel treatment in the homogenization station and ladle furnace;
- to ensure deep desulphurisation of the steel by applying aluminium ($Al_{granular}$) during the tapping, the remelt loss of the alloying additions of $FeSi$ and $FeSiMn$ was reduced, which was manifested with the lower contents of SiO_2 in the ladle slag;
- in the next stage of our research the attention will be focused on confirming these results by producing different steel grades.

Acknowledgements

The work was carried out with the support of the Czech Ministry of Industry and Trade within the frame of the program MPO-TIP and the projects with the reg. No. FR-TI2/319 and reg. No. FR-TI1/240.

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