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EVALUATION OF STEEL DESULPHURIZATION IN THE LADLE DURING THE UTILIZATION OF BRIQUETTING FLUXING AGENTS FOR SLAGS

OCENA RAZŽVEPLJANJA JEKLA V TALILNEM LONCU Z UPORABO BRIKETIRANIH TALIL ZA TVORBO ŽLINDRE

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This paper presents the experience obtained from plant experiments specialized in the usage of three types of fluxing agents for slags based on Al_2O_3. Proper experiments took place during the steel treatment by secondary metallurgy. The objective of the plant experiments was to assess the degree of steel desulphurization and its course. An assessment of the steel desulphurization with the help of basic parameters, such as the degree of desulphurization, the basicity, the content of easily reducible oxides, the proportion of CaO/Al_2O_3 and Mannesmann's index was made. At the same time the behaviour of the fluxing agents and the development of their dissolution in steelmaking slags were assessed.

Keywords: steel desulphurization, slag, fluxing agent, corundum, secondary metalurgy, steel

Članek prikazuje izkušnje, dobljene s preizkusi v železarni, z uporabo treh vrst talil za tvorbo žlindre na osnovi Al_2O_3. Primerni preizkusi so bili izvršeni med obdelavo jekla s sekundarno metalurgijo. Cilj preizkusov v železarni je bil določiti stopnjo razžvepljanja in njegov potek. Z osnovnimi parametri, kot so bazičnost, vsebnost lahko reducirnih oksidov, delež CaO/Al_2O_3 in Mannesmannov indeks, je bilo ocenjeno razžvepljanje jekla. Istočasno je bilo ugotovljeno vedenje talil in nastanek njihovih raztopin v jeklarski žlindri.

Ključne besede: razžvepljanje jekla, žlindra, talilo, korund, sekundarna metalurgija, jeklo

1 INTRODUCTION

Slag is very important during secondary steel treatment. In addition to other effects, it influences the steel desulphurization. The slags in the furnace ladle are formed by fluxes representing lime and fluxing additions (CaF_2 or synthetic slags), subsequent products of steel dezoxidation, corrosion (abrasion) of the lining as well as a certain quantity of passed through furnace slag. These components have different melting temperatures and some of them have melting temperatures that overlap the working temperature of the steel. After the melting of the separate slag components, modifications with the help of slag-making additions with the aim of achieving an optimal chemical composition of the slag and the creation of a so-called refining slag takes place.

The use of fluxing additions represents one of the possibilities to influence the slag properties during secondary metallurgy desulphurization. Their task is to reduce the melting point and also the viscosity of basic steel slags with a view to increasing the slag's reactivity. In this way the desulphurization efficiency can be improved and the physical chemical actions proceeding on the interface slag metal will be accelerated. Presently, fluxing agents based on Al_2O_3 are routinely used. They are produced from pure oxides or various secondary raw materials, i.e., by re-melting, sintering, pelletization, briquetting or using a mixture of separate components. These types of fluxing agents are, nevertheless, used with certain limitations, which come from the technology of their production, their energy intensity and their price[1]. The VŠB-TU Ostrava, FMME, Department of Metallurgy collaborates with industry in the research and development of the briquetting of fluxing agents. These fluxing agents are made from secondary corundum raw materials, which are by-products of the production of electro-melted corundum.

The objective of the work was an assessment of the influence of the chosen fluxing agents for slags based on Al_2O_3 with a view to improving the efficiency of steel desulphurization. The substance of the research consisted of the execution of plant experiments with the use of three fluxing agents for steelmaking slags in a selected secondary metallurgy unit. During the experiments a continuous analysis of the chemical composition of the steel and the slag was performed and the temperature of the steel was measured. At the same time the behaviour of the fluxing agents and the development of their dissolution in steelmaking slags were assessed.

2 COURSE OF THE PLANT EXPERIMENTS

Plant experiments with various fluxing agents for slags were realized in the conditions of a steel plant equipped with numerous secondary metallurgy units:

- homogenization station with the help of inert gas - HS (blowing of argon),
- ladle furnace IR-UT (chemical steel heating),
- ladle furnace LF (heating with an electric arc),
- vacuum station RH.

The course of refining slag production in the ladle is characterized by the gradual mixing and dissolving of separate components. That is why a homogenization station (HS) was chosen for an assessment of the steel desulphurization. In this station only steel homogenization is performed with use of argon, which is blown by a top nozzle (700 l/min) and a bottom nozzle (400 l/min). The acceleration of the dissolving process by warming-up or a modification of the slag's chemical composition does not happen here. Following the chosen parameters of the steel desulphurization and the course of dissolving the fluxing agents in slags makes it possible to measure the possibilities of desulphurization and the behaviour of the separate fluxing agents. The HS makes it possible to improve the following refining parameters of the steel[2]:

- **blowing of argon:**
  - ○ decrease of elements' content:
    - – decrease of C content – no,
    - – decrease of S content – no,
    - – decrease of H content - partially,
    - – decrease of N content – partially,
  - ○ homogenization of steel – yes,
  - ○ exact alloying – partially,
  - ○ guided dezoxidation – no,
  - ○ increasing of microcleanness – partially,
  - ○ modification of inclusions – no,
  - ○ steel desulphurization – no,
  - ○ warming-up of steel – no.
- **blowing of argon + active slag:**
  - ○ decrease of elements' content:
    - – decrease of C content – no,
    - – decrease of S content – partially,
    - – decrease of H content – partially,
    - – decrease of N content – partially,
  - ○ homogenization of steel – yes,
  - ○ exact alloying – yes,
  - ○ guided dezoxidation – partially,
  - ○ increasing of microcleanness – partially,
  - ○ modification of inclusions – no,
  - ○ steel desulphurization – no,
  - ○ warming-up of steel – no.

The proper-plant experiments were realized during the production of S355J steel (ČSN EN 10025–2), which is characterized as an unalloyed structural steel. Its basic chemical composition is given in **Table 1**.

Altogether, 16 heats were performed in the plant conditions with the use of three types of fluxing agents. After tapping, the ladle containing the steel and the created slag was transported to the HS, where the experiment itself started. The whole experiment was planned for 18 min (1080 s). Due to a lack of time the experiment was in some heats shortened to 15 min, i.e., only 900 s. During the steel treatment in the HS samples of steel and slag were taken, whereas samples of steel were taken at intervals of 3 min and slag only at the beginning and at the end of the experiment. The temperature of the steel was measured for each taking of the sample. Afterwards, all the samples of steel were subjected to an analysis, which concerned the content of sulphur. The samples of slags were subjected to an analysis of the basic elements and oxides.

3 CHARACTERISTICS OF THE TESTED FLUXING AGENTS

Three different types of Al_2O_3-based fluxing agents were chosen for optimisation of the slag mode. These fluxing agents differed in terms of their chemical composition, the technology used in their production, the basic raw materials and the grain size. The characteristic of the fluxing agents:

- Fluxing agent A – represents the standard fluxing agent used in the plant conditions. This fluxing agent is formed by crushed slag from the production of ferro-vanadium, the main component of which is Al_2O_3. It is routinely supplied with a grain size from 2 mm to 10 mm.
- Fluxing agent B – represents the developed fluxing agent. It is produced from secondary corundum raw materials, which are in fact by-products from the production of electro-melted corundum (such as dust and sludge), in combination with dolomitic lime and various types of binding agents. The main components are Al_2O_3, $CaCO_3$ (source of CaO) and the binder in the form of water glass (sodium-silica glass). It is made by briquetting and in a standard manner it is delivered as briquettes with dimensions of 60 mm × 50 mm × 30 mm.

Table 1: Chemical composition of the steel grade S355J in mass fractions, *w*/%
Tabela 1: Kemijska sestava jekla S355J v masnih deležih, *w*/%

Element	C	Mn	Si	P	S	Cu	Cr	Ni	Al
Min. content	0.17	1.25	0.15	×××	×××	×××	×××	×××	0.020
Max. content	0.20	1.45	0.55	0.030	0.030	0.20	0.10	0.20	0.045

Fluxing agent A *Fluxing agent B* *Fluxing agent C*

Figure 1: Samples of the three types of fluxing agents used in the experiments
Slika 1: Vzorci treh vrst talil, uporabljenih pri preizkusih

Table 2: Basic chemical composition of the selected fluxing agents
Tabela 2: Osnovna kemijska sestava izbranih talil

Type of fluxing agent	Basic chemical composition, (*w*/%)						
	Al_2O_3	CaO	MgO	FeO	SiO_2	$S_{(Total)}$	Binder
A (standard)	min. 65.0	max. 13.0	max. 15.0	max. 1.5	max. 2.5	max. 2.5	×××
B (developed)	60–70	10–12	5.0–7.0	×××	3.0–4.0	max. 0.01	water glass
C (developed)	60–70	10–12	5.0–7.0	×××	3.0–4.0	max. 0.01	organic

- Fluxing agent C - represents the second variant of the developed fluxing agent. It contains the same basic components in the same proportion as the previous type, but it differs in terms of the type of binder used. In this case an organic binding agent was used. It is also made by briquetting and in a standard manner it is delivered as briquettes with dimensions of 60 mm × 50 mm × 30 mm.

Photographs of the fluxing agents for the plant experiments are shown in **Figure 1**, and the basic chemical composition is given in **Table 2**.

The dosing of the tested fluxing agents during the experiments was as follows. After the processing of the heat in an oxygen converter a slagless tapping into the ladle was performed (for minimization of the FeO content in the ladle slag). During tapping the mixture containing the tested fluxing agent and lime in the ration 1 : 4 was added, then alloying and dezoxidation additions (ferro-alloys, recarburizer and granulated aluminium) were added, too. After tapping, the ladle containing the created slag was transported to the HS, where the experiment itself started.

4 EVALUATION OF THE OBTAINED RESULTS OF THE PLANT EXPERIMENTS

The first evaluation of the refining capabilities of slags with the use of desulphurization was performed by the desulphurization degree ηs *(ETA S)* [3,4]. The degree of desulphurization was defined by the following relation: $(S_{start} - S_{end})/S_{start} \times 100$ %. The evaluation was made for two technological operations:

- Eta S – LP degree of desulphurization from the tapping into the ladle to the transport to the HS,
- Eta S – SHIP degree of desulphurization from the beginning to the end of the processing on the HS.

The results of the degree of desulphurization achieved using slags with various fluxing agents are shown in **Figure 2**. It is evident from this figure that the application of the developed fluxing agents B and C resulted in a lower degree of desulphurization during the steel tapping from the converter into the ladle. During this technological step the fluxes were already added to the ladle and their progressive dissolution and partial desulphurization occurs. A higher degree of desulphurization (approx. 2 times higher), achieved with the fluxing agent A, was apparently caused by the technology of its production. The basis of this fluxing agent consists of the crushed slag from the production of ferro-vanadium. It is therefore possible to assume that the individual components of this material have already been partly melted down. Thanks to these focal points of the molten slags, which may participate in steel desulphurization, are created more rapidly.

In the case of the slags with fluxing agents B and C it is appropriate to bear in mind that they are produced by the briquetting of individual components (electro-melted corundum, lime and binder). These components have high melting points, exceeding the working temperatures of steel (for example, the tapping temperature is approx. 1640 °C). During the tapping of the steel into the ladle the individual components are gradually intermixed and dissolved (fluxes, ferro-alloys, carburizers, etc.), which is accompanied by the formation of a mixture of oxides, which generally have lower melting points than pure oxides. That is why at the mixing, temperature of the liquidus of the oxides mixture gradually decreases, until partial or complete melting of the slag is achieved (and the so-called refining slag is formed).

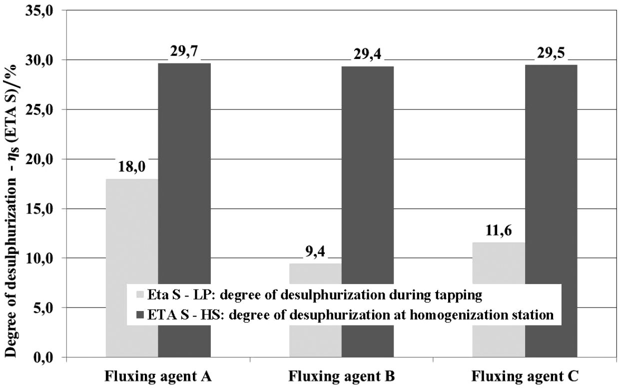

Figure 2: Degree of desulphurization of molten steel
Slika 2: Stopnja razžvepljanja staljenega jekla

The above-mentioned trend of the dissolution of fluxes corresponds to an increase in the degree of desulphurization, which is achieved during steel treatment in the HS. As can be seen in **Figure 2**, all three fluxes with fluxing agents A, B and C show the same high degree of desulphurization. It is therefore possible to assume that in the course of the steel treatment in the HS (approx. 18 min) the slag mixture containing the individual fluxing agents was dissolved and the liquid slag was formed. This liquid slag already significantly participates in the reactions between the slag and the metal.

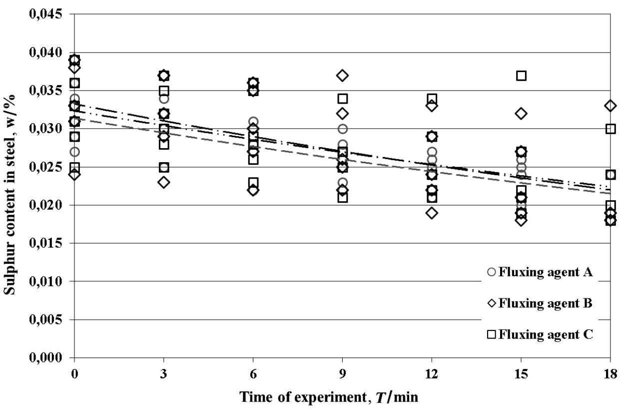

Figure 3: Course of desulphurization in the HS
Slika 3: Potek razžvepljanja v HS

Table 3: Basic statistical parameters of desulphurization achieved with the help of various fluxing agents, *w*/%
Tabela 3: Osnovni statistični parametri za razžvepljanje, doseženi z uporabo različnih talil, *w*/%

Monitored parameters	Fluxing agent A	Fluxing agent B	Fluxing agent C
Maximum value [S]	0.036	0.039	0.039
Minimum value [S]	0.019	0.018	0.018
Average achieved value [S]	0.026	0.028	0.028
Standard deviation	0.004	0.007	0.006
Average value of desulphurization	0.009	0.010	0.010
Variation coefficient	0.165	0.234	0.210

The refining capabilities of slags in the HS were furthermore investigated by an analysis of the development of the desulphurization and of the selected parameters of the slag. The results of the development of the steel desulphurization by slags with various fluxing agents are given in **Figure 3** and in **Table 3**, which contains the basic statistical evaluation of the heat course. The monitored parameters of the slags, such as basicity, content of easily reducible oxides, proportion of CaO/Al_2O_3 and Mannesmann's index, are shown in **Table 4**.[3,4]

Figure 3 gives the obtained values, including the interposed trend curve, separately for individual slags with fluxing agents A, B and C. It is apparent from these results that a drop in the content of the sulphur in the steel is gradual and that the efficiency of the desulphurization by slags with various fluxing agents is almost identical. It also follows from the results in **Figure 3** and **Table 3** that the differences between the individual fluxing agents are negligible, whereas the average value of the desulphurization in the HS within the time interval of 18 min varied from w = 0.009 % (fluxing agent A) to w = 0.010 % (fluxing agents B and C). For an assessment of the coefficient of agreement, a calculation of the variation coefficient for individual slag mixtures was made (**Table 3**). A variation coefficient with values below 0.5 manifests a low degree of variability, whereas the values of the variation coefficient were the following: 0.165 (fluxing agent A), 0.234 (fluxing agent B) and 0.210 (fluxing agent C). These values confirm very similar results during repeated experiments carried out with individual fluxing agents, although these experiments were performed in demanding plant conditions[5].

During the experiment photographs of the created slag from the slag-making additions and the fluxing agent in the ladle were taken, i.e., always at the arrival and departure of the ladle in the HS. The objective was to assess the course of the behaviour and the dissolving of the created steel slags during the steel treatment. A sample of photographs is given in **Figure 4**.

From a comparison of the individual pictures in **Figure 4** *(HS_{start})* it is possible to state that from the tapping from the oxygen convertor to the arrival in the HS the partial dissolution of the mixture representing the slag-making additions and the fluxing agent occurred. This dissolved slag can be considered as active. However, expressive locations containing solid slag are evident in the pictures. It is also proper to state that the whole process of dissolving is significantly influenced by the steel turbulence during tapping. It is evident from the pictures after the ladle's arrival in the HS that during the use of all three fluxing slag additions the creation of active liquid slag in the whole capacity did not course. The arrival time in the HS was approximately 5 min and

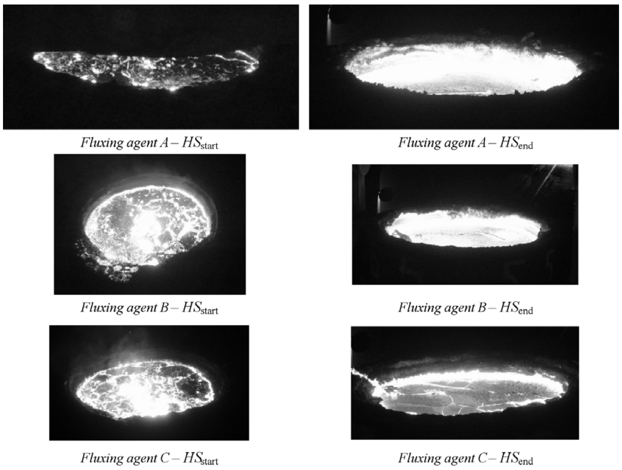

Figure 4: Sample of slag pictures in ladle at the beginning and end of the processing in the HS
Slika 4: Posnetki žlindre v talilnem loncu na začetku in na koncu obdelave na HS

the tapping time was from approximately 5 min to 10 min.

The photographs at the departure of the ladle from the HS in **Figure 4** *(HS_{end})* show the slag-making mixtures after a total processing time of approximately 18 min. The dissolving process was only supported with steel homogenization by the help of the top nozzle and the bottom nozzle. It is also evident that during the use of all three types of fluxing agents the created slag mixtures are totally dissolved and the created steel slag is liquid. This liquid slag can, in a marked way, participate in the desulphurization and steel refinement. It is possible to state that during a visual comparison no difference in the rate of dissolving the slag mixtures was identified. The behavior and consistency of the final slag was on a comparable level, too.

Investigated parameters of the slags, such as the basicity, the content of easily reducible oxides, the proportion of CaO/Al_2O_3 and Mannesmann's index[3,4], are shown in **Table 4**.

From a comparison of the investigated parameters of the slags in the HS from **Table 4** the following findings can be deduced. It follows from a comparison of the individual basicities that sufficiently high values were achieved. The slag mixtures with fluxing agents A, B and C can be classified into the group of medium to highly basic slags. These higher values at the beginning and at the end of experiment in individual slag mixtures contribute to steel desulphurization. This is also obvious from the achieved results of the degree of desulphurization (η_s), as it can be seen in **Figure 2**.

Apart from basicities, the content of easily reducible oxides contained in the slag mixtures was also investigated. In this case a higher content was found. It may be assumed that a certain quantity of easily reducible oxides is formed by partial dezoxidation and by the alloying of the steel. Higher contents (FeO) above $w = 3$ % indicate that in some cases minimum penetrations of the furnace slag into the ladle have occurred. However, at the end of the experiment a decrease in the amount of easily reducible oxides is evident, which may be explained by their reduction by aluminium.

In the case of the proportion of CaO/Al_2O_3 it is apparent that individual slags achieve, at the beginning of the experiment, values >3. However, these values decrease at the end of the individual experiments. It is evident from this development that during the treatment of steel in the HS the remaining part of the fluxing agents is dissolved in the slag. The slag after the treatment in the HS is completely dissolved and liquid.

From a comparison of the Mannesmann's index for slag mixtures it is evident that they vary in the mixture with the fluxing agent A within the interval from 0.15 to 0.30. In the case of slag mixtures with the fluxing agents B and C these indexes fluctuate at the bottom limit of the optimum interval. It is therefore appropriate to pay attention during future experiments to the content of basic oxides and to the proposed proportions of fluxes with use of the fluxing agents B and C.

It can be stated on the basis of the obtained results that the newly developed fluxing agents B and C are comparable with the fluxing agent A, which is used in a standard manner, as they achieved identical values of desulphurization and slag parameters under similar plant conditions. On the basis of currently achieved results, it may therefore be stated that the fluxing agents B and C represent a briquetted mixture of secondary corundum raw materials and that they may possibly fully replace the fluxing agents used so far in a standard manner.

Table 4: Investigated parameters of slags in the HS at the beginning and at the end of the experiment
Tabela 4: Preiskovani parametri žlinder na HS na začetku in na koncu preizkusa

Type of fluxing agent	$B1_{start}$	$B1_{end}$	$B2_{start}$	$B2_{end}$	ERO_{start}	ERO_{end}	C/A_{start}	C/A_{end}	MM_{start}	MM_{end}
A (standard)	3.12	2.80	1.76	1.43	6.55	2.64	3.59	2.83	0.21	0.15
B (developed)	2.98	2.17	1.64	1.17	6.13	1.64	3.01	2.00	0.18	0.11
C (developed)	2.72	2.61	1.66	1.59	6.99	2.36	3.23	2.92	0.18	0.15

Note: B1 – basicity: $B1=(CaO)/(SiO_2)$,
B2 – basicity: $B2=(CaO)+(MgO)/(SiO_2)+(Al_2O_3)$,
ERO – easily reducible oxides: $ERO=(FeO)+(Fe_2O_3)+(MnO)+(Cr_2O_3)+(V_2O_5)+(P_2O_5)$,
C/A – proportion of $C/A=(CaO)/(Al_2O_3)$,
MM – Mannesmann's index: $MM=(CaO/ SiO_2)/(Al_2O_3)$.

5 CONCLUSION

In plant conditions, testing the influence of fluxing agents for steelmaking slags on the efficiency of steel desulphurization during secondary steel refining in the HS was performed. The following findings may be defined from the achieved results of plant experiments:

- during steel tapping from the oxygen converter until arrival at the HS (approx. 10 min to 15 min) partial desulphurization of the steel was achieved. The highest degree of steel desulphurization was achieved by the mixture with the fluxing agent A – approx. 18 %. However, in the case of steel treatment in the HS for approx. 18 min, the achieved degree of steel desulphurization was practically the same for all the slag mixtures – it was approx. 29 %.
- reduction of the sulphur content in steel in the HS is gradual and the efficiency of desulphurization by the slags with different fluxing agents A, B and C is almost identical. The average value of desulphurization for all three types of fluxing agents varied between w = 0.009 % to w = 0.010 % per 18 min.
- during tapping from the oxygen convertor to the arrival in the HS approx. 10 min to 15 min of partial mixture dissolution representing slag-making additions and fluxing agents A, B and C.
- slags after processing for approx. 18 min in the HS are totally dissolved, using of all three types of fluxing agents.
- slag mixtures with fluxing agents A, B and C may be classified according to their basicity into the group of medium to highly basic slags, by which they contribute to the desulphurization of the steel.
- penetrations of the furnace slag into the ladle were detected on the basis of the content of easily reducible oxides.
- in the case of calcium-aluminous proportion it was established that in the course of the experiment in the HS the remaining part of the fluxing agents is dissolved. The slag is completely dissolved and liquid after the treatment.
- from the values of the Mannesmann's index it is evident that in slag mixtures with fluxing agents B and C its values fluctuate at the bottom limit of the optimum interval (approx. 0.3). That is why during future experiments it is necessary to pay attention to the proposed proportions of fluxes.
- the developed fluxing agents B and C are comparable with the fluxing agent A, which is currently used in a standard manner. These fluxing agents B and C represent briquetted mixtures of secondary corundum raw materials and they may fully replace the routinely used fluxing agents, using different secondary raw material and technology of production.
- in the next stage of the research and development of briquetted fluxing agents attention will be focused on a confirmation of these primary results, for example, during the production of different grades of steel, during the use of other secondary metallurgy units or under different plant conditions.

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