EVALUATION OF FLUXING AGENTS EFFECT ON DESULPHURIZATION IN SECONDARY METALLURGY UNDER PLANT CONDITIONS

In the steel industry, a number of fluxing agents based on Al_2O_3 is commonly used. They are produced in different forms. This paper deals with plant results and experiences with the usage of briquetted and sintered fluxing agents for slags based on Al_2O_3. Proper plant heats were processed under conditions of steel plant Vítkovice heavy machinery a.s. during production of steel S34MnV by specific technology: EAF→LF→VCD. During experiments, the basic parameters influencing the steel desulphurization were monitored. Obtained results allow us to make a basic comparison of briquetted fluxing agents produced from secondary raw materials and of sintered fluxing agents, which are produced from pure raw materials.

Key words: steel, secondary metallurgy, desulphurization, fluxing agents, slag regime

INTRODUCTION

In steelmaking industry, the requirements to quality and service properties of steel are continuously increasing. The desulphurization of the steel is one of the basic metallurgical operations taking place during treatment of steel after heat tapping from the electric arc furnace [1], [2]. The next processes of steel refining should be lead under the suitable conditions. It is necessary to have the low viscosity slag with optimal chemical composition for proper desulphurization of the steel. The slag-metal interface should be activated by correctly realized stirring of the bath [3]. The slag-melt surface tension [4] is also very important parameter for speeding up the on-going refining processes. It is appropriate to suggest the optimum proportions of the fluxing agent and the slag-making additions (Al_2O_3:CaO) and to determine the optimal technology of using for achievement of the most suitable conditions of desulphurization and steel refining with the use of slag [1].

The paper extends the work of authors [5] and it focuses on the analysis of plant experiences with the use of two different types of fluxing agents based on Al_2O_3 in the plant conditions of Vítkovice heavy machinery a.s. (hereinafter VHM a.s.) plant. The objective of the plant experiments was to compare the influence of different types of fluxing agents for slags during production of steel grade S34MnV.

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CHARACTERISTIC OF PLANT HEATS AND FLUXING AGENTS

Plant experiments took place under conditions of the VHM a.s. plant during production of steel S34MnV. Its chemical composition is listed in Table 1. This steel is intended for production of crankshafts for ship engines. The steel production is realized by more complicated technology, it is made in this manner: EAF→LF→VCD. Finally, the production is finished by the steel casting into the ingot [6].

Two different types of fluxing agents A and B based on Al_2O_3 were chosen for evaluation of slag regime under plant conditions. The basic chemical composition of both types of fluxing agents is given in Table 2. The fluxing agents differed in their chemical composition, used technology of their production, basic input materials and grain size.

RESULTS AND DISCUSSION

Evaluation of plant results by using fluxing agents A and B was made in a following way. At first, evaluation of influence of fluxing agents for slags on refining capabilities of slag in the ladle by the help of achieved desulphurization degrees η_s *(ETA S)* for chosen technological operations was made [1]:

ETA S_{LADLE} – desulphurization degree from tapping from EAF into the ladle until transport to the ladle furnace LF,

ETA S_{LF-VCD} – desulphurization degree from treatment beginning in the ladle furnace LF until the end of treatment in the vacuum station VCD,

ETA S_Σ – total degree of desulphurization from tapping from EAF until the end of treatment in the station VCD.

Table 1 **Chemical composition of produced steel S34MnV**

Steel grade	Range	Basic chemical composition / wt. %									
		C	Mn	Si	P	S	Cr	Ni	Mo	V	Al
S34MnV	Min.	0,38	1,20	×××	×××	×××	×××	×××	×××	0,06	0,008
	Max.	0,40	1,40	0,10	0,012	0,005	0,30	0,30	0,08	0,10	0,015

Table 2 **Chemical composition of used fluxing agents**

Fluxing agents	Range	Basic chemical composition / wt. %						
		CaO	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	MgO	Na_2O
A	Min.	33,0	51,0	×××	×××	×××	×××	×××
	Max.	35,0	55,0	7,0	2,5	3,0	2,0	×××
B	Min.	10,0	60,0	3,0	×××	×××	5,0	1,0
	Max.	12,0	70,0	4,0	×××	×××	7,0	2,0

Results of desulphurization degree of steel by the help of fluxing agents A and B are shown on Figure 1. During the technological operation tapping from EAF until transport to the ladle furnace LF, a lower degree of desulphurization was achieved - *ETA S$_{LADLE}$*. Values 21 % (fluxing agent A) and 28 % (fluxing agent B) were achieved. It can be explained with the gradual, only beginning, solution of separate slag-making additions (representing lime and fluxing agents), in a short time interval running approx. 8 to 11 minutes.

During following operation in LF to VCD multiple growth of desulphurization degree - *ETA S$_{LF-VCD}$* in comparison with desulphurization during tapping into the ladle - *ETA S$_{LADLE}$* happens. The values 87 % (fluxing agent A) and 88 % (fluxing agent B) were obtained. Strong growth of desulphurization degree can be explained with the total solution of slag-making additions. Modification of chemical composition of slag by the help of the second dose of slag-making additions (lime, fluxing agent, material for lining protection, Al and CaC$_2$) presents another influence. Created slag mixture can be defined as a refining slag.

The total degree of desulphurization - *ETA S$_\Sigma$* was 89 % (fluxing agent A) and 92 % (fluxing agent B). It is evident from the resulting degrees of desulphurization *ETA S$_\Sigma$* that during using fluxing agents A and B a in effect the same desulphurization degree of steel was achieved. It is proper to point out that each type of fluxing agent A and B is produced from different raw materials and by different technology of production.

Next, the evaluation of slag regime in the ladle was made. The monitored parameters of slags [5, 7, 8] that influence the desulphurization capabilities are shown on Figure 2 to Figure 6.

Figure 2 presents the influence of basicity – B on desulphurization. It is obvious that the initial basicity after the first dose of slag-making additions achieves the values 5,6 and 7,7. The next growth to the values 8,1 and 9,2 occurs with the second dose of slag-making additions. These slags can be identify as highly basic slags, namely already at the beginning of treatment within the secondary metallurgy.

It is also evident from Figure 2 that a gradual fall of desulphurization degree during basicity growth occurs.
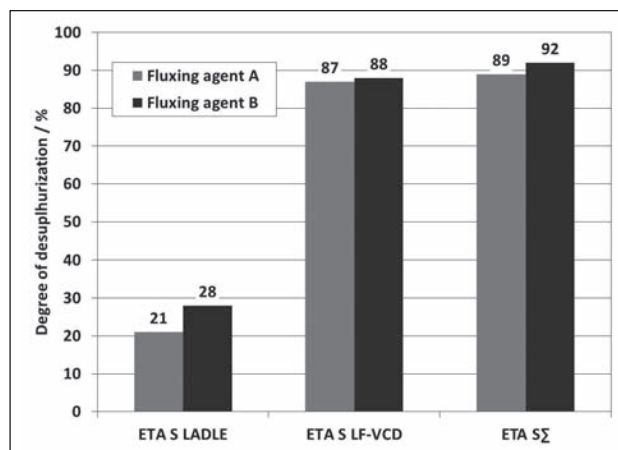

Figure 1 Achieved degrees of desulphurization of the steel grade S34MnV
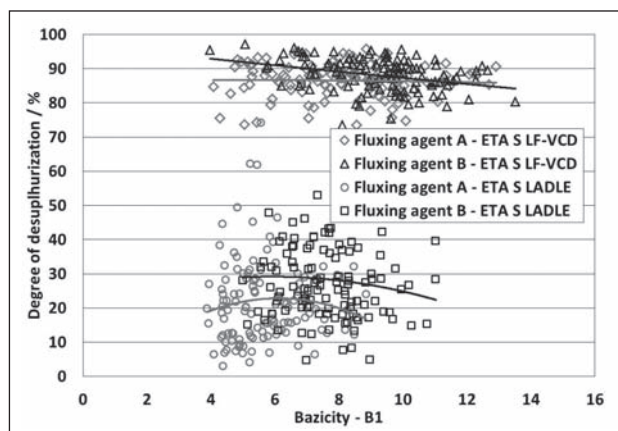

Figure 2 Dependence of degree of desulphurization on the narrow basicity - B

This tendency can be explained by the influence of higher contents of CaO in the slag which leads to its thickening, decrease of refining capabilities and achievement of lower degrees of desulphurization. It can be expected that the total solution of slag mixtures together with modification of chemical composition occurs during the treatment in the ladle furnace LF which was shown with the growth of basicity and it helped to the higher degree of steel desulphurization.

Decrease of content of easily reducible oxides is evident from Figure 3 for both fluxing agents A and B. It is
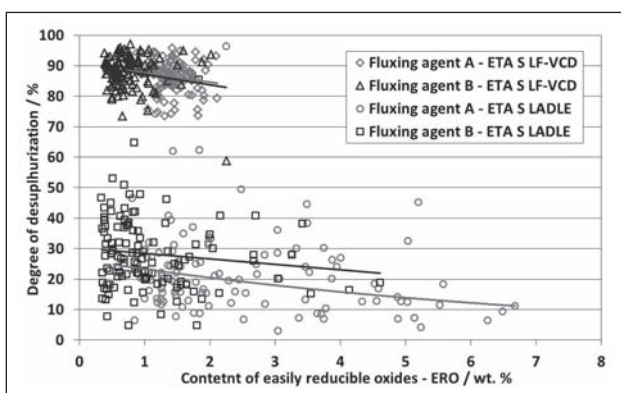
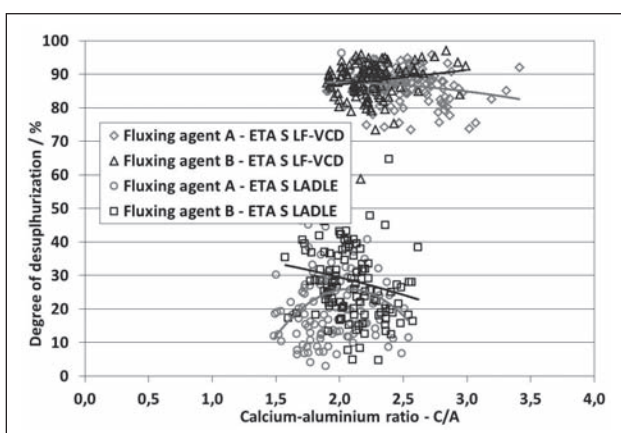**Figure 3** Dependence of degree of desulphurization on the content of easily reducible oxides – ERO

Figure 4 Dependence of degree of desulphurization on the calcium-aluminium ratio – C/A

Figure 5 Dependence of degree of desulphurization on the Mannesmann´s index – MM
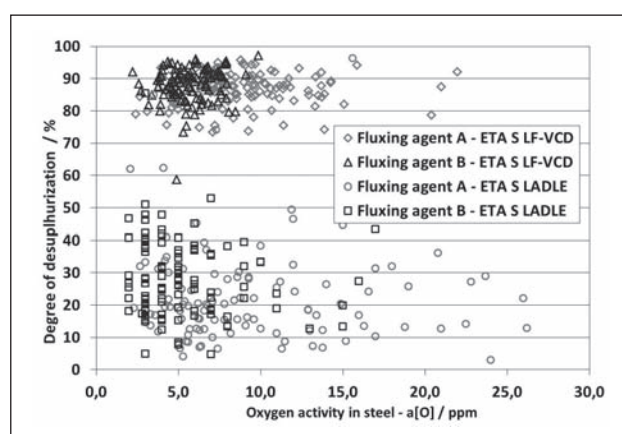
Figure 6 Dependence of degree of desulphurization on the oxygen activity in steel – $a_{[O]}$

possible to explain by their aluminium reduction and by CaC_2 added in the ladle furnace LF during treatment. In this case, reduction of mentioned oxides to contents 1,40 and 0,77 wt. % was achieved. This modification of chemical composition of slags in the ladle furnace LF made it possible to reach the high degree of desulphurization *ETA S$_{LF-VCD}$* (89 % to 92 %) and it supported the deep steel desulphurization (S$_{Max.}$ 0,005 wt. %).

The next parameter presents the CaO/Al_2O_3 proportion. The optimum value of this parameter should be higher than 2,0 because higher contents of Al_2O_3, namely > 25 wt. %, are required in the refining slag. It is evident from Figure 4 that during tapping and transport to the ladle furnace LF values 1,94 and 2,11 were achieved. These values represent the bottom limit of the optimum ratio C/A which was created with the first dose of slag-making additions. However, the separate components don't need to be totally dissolved yet.

It is also evident from Figure 4 that these values go up to 2,50 and 2,25 at the end of treatment in secondary metallurgy units. This growth is caused by the second dose of slag-making additions and by the solution of separate components of slag in the ladle furnace LF. It is obvious from this development that during secondary metallurgy targeted modification of chemical composition of slags for achievement of optimum proportion C/A supporting the refining and desulphurization capabilities of slag occured.
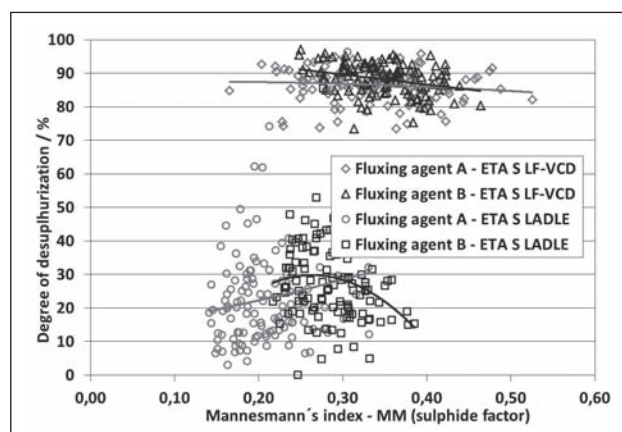
Following monitored parameter is Mannesmann's index (so-called sulphide factor). The optimum value of mentioned parameter should be within the limits 0,15 and 0,30. It is evident from Figure 5 that the fluxing agents A and B reach values 0,21 and 0,29 with the partial solution of the first dose of slag-making additions in the ladle. However, it is obvious from Figure 5 that the addition of next slag-making additions during the beginning of treatment in the ladle furnace LF shown with the values growth to 0,34 and 0,35. These values present the upper limit of the Mannesmann's index. The decrease of desulphurization degree came out with the increasing Mannesmann's index during monitoring of this parameter (see Figure 5). It is related to the increased thickening of refining slag.

It was found from the results of oxygen activity in steel (see Figure 6) that decrease of oxygen activity occurs with the first dose of dezoxidation additions during tapping from values approx. 400 - 800 ppm measured in EAF just before tapping to values approx. 10,5 and 5,4 ppm measured during the beginning of steel treatment in the ladle furnace LF. The next decrease happens with the addition of dezoxidation agents to the values 9,0 and 5,7 ppm in the following treatment in secondary metallurgy units. In this case, it shoud be noticed, that specific dispersion and a weaker decrease of oxygen activ-

ity happen which is caused by production technology EAF→LF→VCD when deep cogulative steel dezoxidation isn't made.

CONCLUSIONS

In plant conditions of the steel plant VHM a.s., a series of experimental heats using two types of fluxing agents A and B during production of steel grade S34MnV was made. The aim was to assess the effectivity of steel desulphurization.

From the obtained results of plant experiments can be defined that the fluxing agent B presenting the briquetted mixture of secondary corundum raw materials can adequately replace the fluxing agent A formed by sintered mixture of natural raw materials.

In the next stage of research of fluxing agents and their influence on creation of refining slag, the attention will be focused on confirmation of these plant results during production of different grades of steel.

Acknowledgements

REFERENCES

[1] A. Ghost, A. Chatterjee, Ironmaking and Steelmaking: Theory and Practice, PHI Learning Private limited, 2008, 472 p.

[2] J. Kijac, M. Borgon, Desulphurization of steel and pig iron, Metalurgija, 47 (2008) 4, 347-350.

[3] K. Michalek, K. Gryc, J. Moravka, Physical Modelling of Bath Homogenisation in Argon Stirred Ladle, Metalurgija, 48 (2009) 4, 215-218.

[4] R. Dudek, Ĺ. Dobrovsky, J. Dobrovska, Study of Surface Tension of Inorganic Melts Based on Their Chemical Composition and Temperature, Metalurgija, 48 (2009) 4, 239-242.

[5] L. Socha, J. Bažan, P. Machovčák, A. Opler, P. Styrnal, J. Melecký, Plant Experiments with Steel Desulphurization by Secondary Metallurgy with use of Briquetted Fluxing Agents in the Steelplant Vítkovice heavy machinery a.s., Hutnické listy, LXV (2012) 2, 8-13 (in Czech).

[6] http://www.vitkovicemachinery.com/

[7] M. Allibert, et al. Slag atlas. 2nd Edition, Düsseldorf: Verein Stahleisen GmbH, 1995, 616 p.

[8] K. Gryc, K. Stránský, K, Michalek, et al., A Study of the High-Temperature Interaction between Synthetic Slags and Steel. Materials and Technology, 46 (2012) 3, 59-62.