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EVALUATION OF INFLUENCE OF BRIQUETTED SYNTHETIC SLAGS ON SLAG REGIME AND PROCESS OF STEEL DESULPHURIZATION

OCENA WPŁYWU ZASTOSOWANIA BRYKIETOWANYCH ŻUŻLI SYNTETYCZNYCH NA PRZEBIEG PROCESU ODSIARCZANIA STALI

This paper presents the industrial results of evaluation of efficiency of synthetic slags during the treatment of steel at the equipment of the secondary metallurgy under conditions of the steel plant VÍTKOVICE HEAVY MACHINERY a.s. The aim of the heats was to assess the influence of the briquetted and sintered synthetic slags based on Al_2O_3 aiming the course of the steel desulphurization and slag regime during the production and treatment of steel grade 42CrMo4 with the technology EAF→LF→ VD. Within the plant experiments, basic parameters influencing the steel desulphurization and slag regime were monitored: desulphurization degree, basicity, content of easily reducible oxides, proportion of CaO/Al_2O_3 and Mannesmann's index. Obtained results allowed to compare the steel desulphurization and to evaluate the slag regime. It was proved that the synthetic slag presenting the briquetted mixture of secondary corundum raw materials can adequately replace the synthetic slag created from the sintered mixture of natural raw materials.

Keywords: synthetic slag, slag regime, desulphurization, secondary metallurgy, steel

W pracy tej przedstawiono przemysłowe wyniki oceny efektywności zastosowania żużli syntetycznych podczas obróbki pozapiecowej stali w zakładzie VÍTKOVICE HEAVY MACHINERY a.s. Celem badań był a ocena wpływu brykietowanych i spiekanych żużli syntetycznych opartych na Al_2O_3 – na przebieg odsiarczania stali i żużla podczas produkcji i obróbki stali 42CrMo4, zgodnie z technologią EAF → LF → VD. Podczas eksperymentów w zakładzie, monitorowano podstawowe parametry wpływające na odsiarczania stali i żużla: stopień odsiarczania, zasadowość, zawartość tlenków łatwo redukowalnych, stosunek CaO/Al_2O_3 oraz indeks Mannesmann'a. Uzyskane wyniki pozwoliły na porównanie stopnia odsiarczania stali w kontekście zastosowanych żużli. Wykazano, że syntetyczny żużel składający się z brykietowanej mieszaniny wtórnego korundu, może zastąpić syntetyczny żużel otrzymywany ze spieku mieszaniny surowców naturalnych.

1. Introduction

The task of refining slag in the secondary metallurgy is to increase the cleanness of liquid steel, i.e. to absorb and chemically bind sulphur from the steel, to absorb the non-metallic inclusions, to protect the steel from the atmosphere and from the heat losses at the minimum corrosion of ladle lining. Ladle slag is made from the products of steel dezoxidation, slag-making additions, products of corrosion of ladle lining and it is also created by a certain amount of passed through furnace slag. The additions purposefully added into the slag ensure its required chemical composition, liquidity and its ability to refine the steel. It is mostly lime, CaC_2 and synthetic slags commonly used today [1, 2, 3].

Synthetic slags usually contain Al_2O_3, CaO, MgO, SiO_2 and minimum of FeO, Fe_2O_3, MnO and sulphur on the contrary. Improvement of the physical and chemical properties of ladle slags is the task of synthetic slags added into the ladle. Mentioned requirements influence the basicity, slag viscosity and interface tension. However, these properties are also dependent on chemical composition of synthetic slag and on its heat temperature [4, 5].

Synthetic slag influences the properties of ladle slag not only with its chemical composition but also with phase composition and grain size which shows in the speed of ladle slag creating. However, chemical and phase composition, manner of the preparation, production and grain size of mentioned synthetic slags are different. Nowadays, synthetic slags are made not only from natural raw materials but also from various secondary raw materials, namely by re-melting, sintering, pelletization, briquetting or by pure mixture of separate components. However, proper production is connected with the purpose of the synthetic slag application, further with the raw materials resources from which the slag is made [6, 7].

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This paper extends the work by authors [8, 9] and it focuses on analysis of plant experience during the utilization of two different types of synthetic slag based on Al_2O_3 under the condition in the steel work VÍTKOVICE HEAVY MACHINERY a.s. (hereinafter VHM a.s.) The aim of plant experiments was to compare the influence of different types of synthetic slags during production of steel grade 42CrMo4.

2. Characteristics of plant experiments and synthetic slags

Plant experiments with synthetic slags were realized under the conditions of steel work VHM a.s. Proper production process occurred in the following way: tapping into the ladle (LADLE) was made after the treatment of the heat in the electric arc furnace (EAF). The main part of slag-making additions containing mixture of lime and tested synthetic slags was prepared in the ladle. After tapping, the ladle containing steel and created slag was transported to the ladle furnace (LF) where the targeted steel modification by the help of addition of the second part of slag-making additions presenting lime, tested synthetic slag, material for slag line protection, aluminium in different forms (cracked and granular) intended for decrease of contain of easily reducible oxides and for slag modification was made. Subsequently after steel treatment in the ladle furnace, the ladle was transported to the vacuum station (station VD). Finally, the production process is finished by the steel casting into the ingot [10, 11].

Proper experiments were realized during production of steel grade 42CrMo4 which is described as low-alloyed noble chromium-molybdenum steel intended for coating of steel. Its chemical composition is given in Table 1.

Within the plant experiments, two different types of synthetic slags based on Al_2O_3 were chosen for the creation of ladle slag. Basic chemical composition of both synthetic slags A and B for plant experiments are given in Table 2. These synthetic slags differed in the basic raw materials, used technology of their production, chemical composition and grain size:

- **synthetic slag A**: is produced from natural raw materials, such as bauxite, lime or dolomite and the main component is Al_2O_3. Proper production is realized in the rotary furnace where sintering happens and porous granular synthetic slag with the grain size from 5 to 15 mm is a result,
- **synthetic slag B**: is produced from secondary corundum raw materials which are by-products from the production of electro-melted corundum (such as for example dust and sludge) in the combination with dolomitic lime and binding agent (water glass). The main components are Al_2O_3 and $CaCO_3$ which is a source of CaO. This type of slag is made by briquetting. In standard manner, it is delivered in the form of briquettes with dimensions 60×50×30 mm.

During plant experiments slag-making additions were added in two same doses. However, they differed in the rate of separate components. The main part of synthetic slags was added during tapping with lime in different rates.

In case of synthetic slag A, the rate of slag to lime was 1:1.2 and in case of synthetic slag B was the rate 1:1.9. These different rates come out from their chemical composition. Achievement of similar content of Al_2O_3 in the slag during secondary metallurgy is the reason. In the second dose, synthetic slags were minimally used during steel refining in the ladle furnace (LF). Above all, lime was used for modification of chemical composition and material for slag line protection because of decrease of ladle lining abrasion. Aluminium in different forms intended for modification of chemical composition of slag is the last added material.

Altogether ca. 155 heats with both types of synthetic slags were made under plant conditions. During secondary metallurgy, samples of steel and slag were taken, namely in following technological places: in the ladle after tapping from EAF (sample LADLE), at the beginning of treatment in the ladle furnace (sample LF) and at the end of treatment in the vacuum unit (sample VD). In case of steel, analysis of sulphur content was especially made. In the slag samples, analysis aiming the sulphur content and basic types of oxides was made.

TABLE 1

Chemical composition of produced steel 42CrMo4

Steel grade	Range	Basic chemical composition (wt. %)							
		C	Mn	Si	P	S	Cr	Mo	Al
42CrMo4	Min.	0.40	0.60	0.20	×××	×××	0.90	0.15	0.015
	Max.	0.44	0.70	0.30	0.012	0.005	1.10	0.25	0.030

TABLE 2

Chemical composition of used synthetic slags

Synthetic slag	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

3. Evaluation and discussion of results

Evaluation of tested synthetic slags A and B was concentrated on abilities of steel desulphurization. At first, influence of synthetic slags was compared by the help of achieved degree of steel desulphurization η_s *(ETA S)*. Mentioned parameter is defined by following relation [12, 9]:

$$\eta_S = \frac{[S_{START}] - [S_{END}]}{[S_{START}]} \cdot 100 \tag{1}$$

Proper evaluation was made for following technological operations:

- **Eta S LADLE** – desulphurization degree from tapping into the ladle until transport to the ladle furnace LF,
- **Eta S LF-VD** – desulphurization degree from the beginning of treatment in the ladle furnace LF until the end of treatment in the vacuum station VD,

– **Eta S total** – total degree of desulphurization from tapping into the ladle until the end of treatment in the station VD.

Results of the desulphurization degree are given in the Fig. 1 and they present average values of separate technological operations which were completed with the values presenting determinant difference.

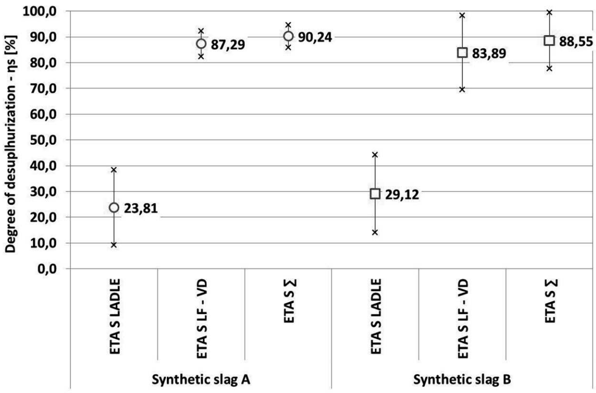


Fig. 1. Achieved degrees of desulphurization

It follows from Fig. 1 that in case of synthetic slag A desulphurization degree 24% was achieved during tapping and transport to the ladle furnace LF, 87% during secondary metallurgy (LF to VD) and the total degree of desulphurization was 90%.

In case of synthetic slag B, desulphurization degree 29% was achieved in the ladle, from the tapping until the transport to the ladle furnace LF, 84% during secondary metallurgy (from LF to VD) and the total achieved degree of desulphurization was 89%. From the comparison of desulphurization degree *ETA S LADLE* it is possible to state that in case of both types of synthetic slags similar low degree of desulphurization occurred. It can be explained with gradual solution of separate slag-making additions (created especially from lime and synthetic slag A or B) in a short time interval (running for a few minutes).

During following technological operation *ETA S LF – VD* (treatment in LF to VD), three times higher growth of desulphurization degree occurs. In case of this operation desulphurization degrees are also comparable for both tested synthetic slags A and B. Strong growth of desulphurization degree can be explained with the total solution of slag-making slags and with the modification of the chemical composition of the slag by the help of the second dose of slag-making additions (lime, synthetic slag, material for lining protection, Al for reduction and modification of the composition of the ladle slag). Created ladle slag at usage of both synthetic slags can be defined as a liquid slag that participates in the reactions between slag and metal in an important way.

From the comparison of resulting degrees of desulphurization *ETA S total* it is evident that during secondary metallurgy the influence of both synthetic slags A and B on steel desulphurization is practically the same (90% and 89%), although each type of synthetic slag is made from different raw materials and with different technology of production.

The influence of tested synthetic slags on desulphurization abilities of slags during steel treatment in the secondary metallurgy was further evaluated with the analysis of the influence of chosen parameters of slags on desulphurization degree. Basicity, content of easily reducible oxides, proportion of CaO/Al_2O_3 and Mannesmann's index belong to the monitored parameters. These parameters were defined by the help of following relations [13, 12, 9]:

$$B1 = \frac{(CaO)}{(SiO_2)} \tag{2}$$

$$B2 = \frac{(CaO) + 2/3\,(MgO)}{(SiO_2) + (Al_2O_3)} \tag{3}$$

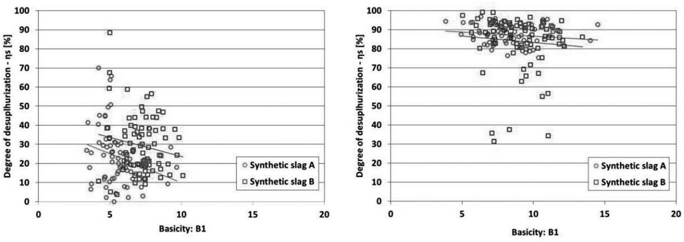
$$ERO = (FeO) + (Fe_2O_3) + (MnO) + (Cr_2O_3) + (V_2O_5) + (P_2O_5) \tag{4}$$

$$C/A = \frac{(CaO)}{(Al_2O_3)} \tag{5}$$

$$MM = \frac{(CaO)/(SiO_2)}{(Al_2O_3)} \tag{6}$$

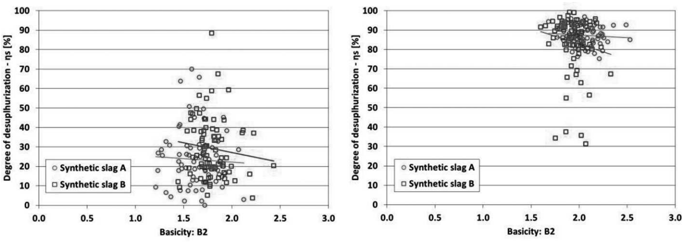
In the Fig. 2 to Fig. 6, monitored parameters of slags are given which influence the desulphurization abilities in an important way. Fig. 2a presents the basicity of the slag mixtures. These slag mixtures can be identify as highly basic slags with the average basicity 5.51 and 7.25. In the case of wide basicity B2 (see Fig. 3a), it can be spoken about medium basic slags with the average basicity 1.63 and 1.8. It is also evident from Fig. 2a and Fig. 3a that gradual decrease of desulphurization degree during increase of basicity occurs. This tendency can be explained with the influence of higher contents of CaO in the slag which leads to its thickening, decrease of refining capabilities and to achievement of lower degrees of desulphurization. It is also obvious from Fig. 2b and Fig. 3b that during the treatment in the ladle furnace LF the total solution of slag-making additions together with the modification of the chemical composition occurred. This led to the increase of average values of basicity B1 to 8.28 and 9.16 and in the case of basicity B2 to values 2.08 and 1.93 and it helped to the deep desulphurization of steel. This tendency is evident also from the achieved degree of desulphurization of both synthetic slags A and B in the Fig. 1.

The next monitored parameter was the content of easily reducible oxides. In this case, appearance of average contents 1.92 and 0.83 wt. % in the case of both synthetic slags A and B is obvious from Fig. 4a. It can be supposed that certain amount of mentioned oxides is made by the partial dezoxidation and alloying of steel. The higher contents (FeO) over 3 wt. % indicate that the ladle slag passed through into the ladle.



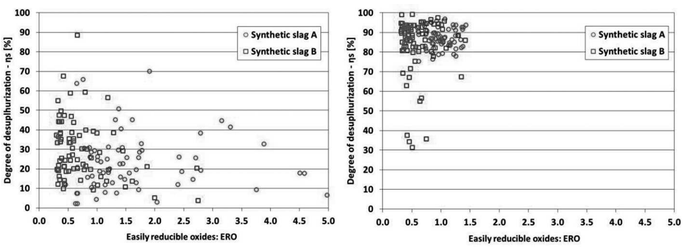
a) Entrance LF *b) The end of treatment VD*

Fig. 2. Dependence of desulphurization degree on narrow basicity – B1



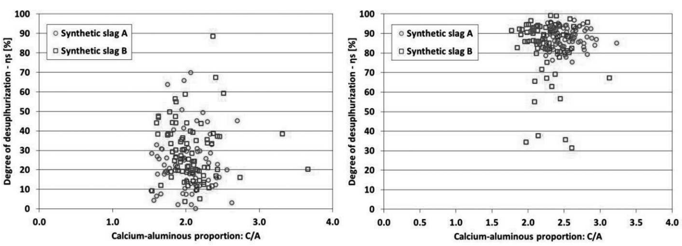
a) Entrance LF *b) The end of treatment VD*

Fig. 3. Dependence of desulphurization degree on wide basicity – B2



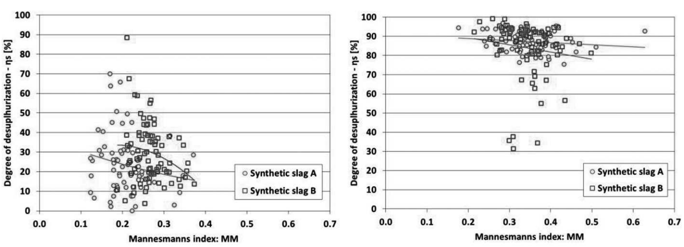
a) Entrance LF *b) The end of treatment VD*

Fig. 4. Dependence of desulphurization degree on content of easily reducible oxides – ERO



a) Entrance LF *b) The end of treatment VD*

Fig. 5. Dependence of desulphurization degree on calcium-aluminium proportion – C/A



a) Entrance LF *b) The end of treatment VD*

Fig. 6. Dependence of desulphurization degree on Mannesmann's index – MM (sulphide factor)

These exceptional cases were found by both slag mixtures which can be seen in Fig. 4a. Evident decrease of content of easily reducible oxides is obvious from Fig. 4b. It can be explained with their reduction by the help of aluminium added in the ladle furnace LF at the beginning of the treatment. In this case, reduction of mentioned oxides to the average contents 0.99 and 0.60 wt. % made it possible to achieve the high degree of desulphurization (87% and 81%) and it supported the deep steel desulphurization during utilization of both synthetic slags A and B.

Subsequently, the calcium-aluminium proportion C/A was monitored. The optimum value of this parameter should be in the range from 1.7 to 2.3 because higher contents of Al_2O_3 are required in the refining slag, namely >25 wt. %. It is evident from Fig. 5a that both slag mixtures achieve similar average values 2.02 and 2.08 during tapping and transport to the ladle furnace LF. It represents the bottom limit of optimum proportion (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. But it is evident from Fig. 5b that these average values increase to 2.54 and 2.26 at the end of treatment in the secondary metallurgy. This growth is caused by the second dose of slag-making additions and with the solution of separate components of slag in the ladle furnace LF. From this development it is evident that during the steel treatment in the equipment of secondary metallurgy (in the station LF to VD) a targeted modification of chemical composition of slags occurs. In this way, an optimum proportion of CaO/Al_2O_3 (C/A) supporting the refining and desulphurization capabilities of slag mixtures was achieved.

The last monitored parameter is Mannesmann's index (so called sulphide factor). The optimum value of this parameter should be in the range from 0.15 to 0.30. It is obvious from Fig. 6a that with the partial solution of the first dose of slag-making additions in the ladle both slag mixtures achieve the average values 0.18 and 0.27. This is the optimum range. However, it is evident from Fig. 6b that addition of another slag-making additions at the beginning of the treatment in the ladle furnace LF shown with the growth of average values to 0.34 and 0.35 which represents the optimum upper limit of the mentioned parameter. Also at the monitoring of this parameter (Fig. 6a and Fig. 6b) decrease of desulphurization degree came out with the increasing Mannesmann's index. It is related to the increased thickening of refining slag.

4. Conclusions

Series of experimental heats with the using two types of synthetic slags was made under the plant conditions of the steel work VHM a.s. The aim was to assess the efficiency of steel desulphurization during treatment of steel 42CrMo4 during processes of the secondary metallurgy. According to the obtained results of plant experiments, following findings can be defined:

– during the technological operation LADLE, a low degree of desulphurization ETA S LADLE was found out, namely 24% (synthetic slag A) and 29% (synthetic slag B). During following operation in the station LF to VD, multiple growth of desulphurization degree ETA S LF – VD compared to the desulphurization during tapping into the ladle, namely 87% and 84% was monitored,

- total degree of desulphurization ETA S total for both synthetic slags was 90% and 89%,
- based on obtained values of basicity, it is possible to include the created slag mixtures to the group of highly to medium basic slags. The next growth of basicity occurs with the second dose of slag-making additions which helps to the achievement of deep desulphurization of steel,
- according to the results of content of easily reducible oxides, minimum penetration of ladle slag into the ladle was determined. Except that, positive influence of reduction of mentioned oxides with the additions of aluminium in the ladle furnace LF was confirmed which shown in the content decrease of monitored oxides,
- based on results of calcium-aluminium proportion, it was found out that the value 0.20 was achieved with the first dose of slag-making additions (lime and synthetic slag). This value can be considered as the bottom limit of optimum range of proportion C/A. With the addition of the second dose (lime and aluminium) the value was further increased by ca. 20%,
- it follows from the values of Mannesmann's index that slag-making mixtures of both synthetic slags move in the optimum range from 0.15 to 0.30. The upper limit 0.35 is achieved with the second dose of slag-making additions,
- it was found from achieved plant results that synthetic slag B presenting the briquetted mixture of secondary corundum raw materials can adequately replace the synthetic slag A formed by sintered mixture of natural raw materials, namely according to the results of steel desulphurization, values of desulphurization degree and other monitored parameters.

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