THE INFLUENCE OF BRIQUETTED SYNTHETIC SLAGS ON STEEL REFINING IN LADLE

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Abstract
Synthetic slags are used during steel treatment in the ladle from the viewpoint of effective refinement. Their basic task is formation of active slag for improvement of kinetic conditions of refining processes. In the steel industry, a number of synthetic slags based on Al2O3 are used which are produced from natural or secondary raw materials in different forms. However, the use of synthetic slags is influenced by the choice of used raw materials, by production technology and by final chemical composition. This paper shows plant results and experience with the utilization of briquetted synthetic slags based on Al2O3 and containing different amount of Cr2O3. Trial plant heats were realized during steel treatment under the conditions of steelwork VÍTKOVICE HEAVY MACHINERY a.s. The main aim of these heats was assessment of the plant results with utilization of two types of synthetic slags with different chromium content and the evaluation of the increase of chromium content in steel as well as the course of desulphurization during steel treatment.

Keywords: synthetic slag, steel, desulphurization, secondary metallurgy

1 Introduction
Slag mode in secondary metallurgy significantly influences the final quality of the produced steel, particularly from the perspective of achieved desulphurisation of steel. One of the possibilities of influencing the slag mode is application of synthetic slags into ladle slag formed from added slag-making additions [1, 2, 3]. Process of formation of ladle slag is, however, comparatively demanding and it depends on quantity of slag-making additions, method of steel desulphurisation, intensity of stirring, corrosion (wear) of the ladle lining and quantity of the flown furnace slag. The formed mixture of individual oxides represents the ladle slag, the composition of which considerably influences viscosity and also its refining capacity [4, 5]. Synthetic slags are currently manufactured from natural or secondary raw materials and they usually contain Al2O3, CaO, MgO, SiO2, and on the other hand only minimum FeO, Fe2O3, MnO, Cr2O3 and sulphur. Thus prepared mixtures of basic raw materials are further processed to synthetic slags in various forms (e.g. re-melted, sintered, pelletised, lump or powder mixtures). All above mentioned types of synthetic slags are, however, used with certain limitations, which ensue from selection of the used raw materials and production technologies [6, 7, 8].
The paper is a follow-up of the works of the authors [9, 10, 11, 12] and it presents industrial results and experience with use of briquetted synthetic slags based on Al2O3 and containing different contents of Cr2O3 varying from 0.3 to 3.0 wt. % in conditions of the steel-shop at the VÍTKOVICE HEAVY MACHINERY a.s. (hereinafter VHM a.s.). The objective of industrial experiments consisted in comparison of the results achieved at use of both types of synthetic slags with focus on the evolution of desulphurisation and assessment of influence of oxide Cr2O3 on increase of chromium in steel during process of secondary metallurgy.

2 Characteristics of industrial experiments in conditions of the steel-shop VHM a.s.

Industrial experiments with synthetic slags with different contents of Cr2O3 were realised at steel treatment on secondary metallurgy units in conditions of the steel-shop at the VHM a.s. Production process ran in the following manner: during tapping of steel from EAF into ladle deoxidation of steel (Al_ingot), deactivation of slag (Al_skimming and CaC2), alloying and addition of the main part of slag-making additions (mixture of lime and tested synthetic slags with different contents of Cr2O3) take place. The ladle with steel and formed slag was after tapping transported to the ladle furnace LF, where targeted modification of slag in the ladle was performed by addition of the second part of slag-making additions (lime and synthetic slags), material for protection of slag line (approx. 45 % of MgO), calcium carbide (CaC2) and aluminium in various forms (Al_granular) determined for reduction of contents of easily reducible oxides and modification of ladle slag. Afterwards, after treatment of steel in the ladle furnace LF, the ladle was transported to the vacuum unit VD. Production process was completed by casting of steel into ingots [13].

Proper industrial experiments were realised at production of steel grade St52-3, which was produced by basic technology, consisting of the following procedure: EAF→LF→VD. Production chemical composition of steel is given in Table 1. During the evaluated period we monitored altogether 184 heats of the steel grade St52-3, with use of both types of synthetic slags different contents of Cr2O3.

Table 1 Production chemical composition of steel grade St52-3

<table>
<thead>
<tr>
<th>Grade</th>
<th>Range</th>
<th>Chemical composition (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>St52-3</td>
<td>Min.</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>Max.</td>
<td>0.22</td>
</tr>
</tbody>
</table>

Table 2 Production chemical composition of steel grade St52-3

<table>
<thead>
<tr>
<th>Type of synthetic slag</th>
<th>Range</th>
<th>Chemical composition (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Al2O3</td>
</tr>
<tr>
<td>A65C11VS</td>
<td>Min.</td>
<td>60.0</td>
</tr>
<tr>
<td></td>
<td>Max.</td>
<td>70.0</td>
</tr>
<tr>
<td>A65C10VS-Cr</td>
<td>Min.</td>
<td>60.0</td>
</tr>
<tr>
<td></td>
<td>Max.</td>
<td>70.0</td>
</tr>
</tbody>
</table>

For evaluation of influence of Cr2O3 on the slag mode in industrial conditions two types of briquetted synthetic slags A65C11VS and A65C10VS-Cr based on Al2O3 (60 to 70 wt. %) were chosen. Both types of synthetic slags are produced from secondary corundum raw materials with
different contents of $\text{Cr}_2\text{O}_3$ in corundum raw material (0.3 and 3.0 wt. %) in combination with dolomitic lime and binder (water glass). The main component is formed by $\text{Al}_2\text{O}_3$ and $\text{CaCO}_3$, which serve as source of CaO. Both types of synthetic slags are manufactured by briquetting and they are delivered in a standard manner in the form of briquettes with dimensions $60 \times 50 \times 30$ mm. Basic chemical composition of synthetic slags is presented in Table 2.

3 Results

Evaluation of influence of synthetic slags containing $\text{Cr}_2\text{O}_3$ on the evolution of desulphurisation and increase of chromium in the steel was realised in several steps. First, evaluation of used synthetic slags according to their ability to desulphurise steel with use of the degree of desulphurisation $\eta_s$ was made. The method of calculation of mentioned parameter is based on the works [9, 10, 14]. Results of degrees of desulphurisation ($\eta_s$) are presented in Fig. 1a and Fig. 1b and they represent the degrees of desulphurisation for individual technological operations, which took place during treatment of steel.

![Fig. 1](image-url)  

**Fig. 1** Achievement of the degree of desulphurisation at individual stages of steel treatment
It is evident from the results (Fig. 1a and Fig. 1b), that individual average values of degrees of desulphurisation representing different technological operations of steel treatment (EAF→LF→VD) achieved for the used synthetic slags A65C11VS and A65C10VS-Cr different trends. That's why results of degrees of desulphurisation were completed with achieved contents of sulphur at individual stages of treatment (Fig. 2a and Fig. 2b).

It follows from the results (Fig. 1a and Fig. 1b) that overall average degree of desulphurisation $\eta_S\sum$ was for both synthetic slags A65C11VS and A65C10VS-Cr approx. 93 %, which corresponds to the decrease of sulphur (Fig. 2a and Fig. 2b) from the average initial contents of sulphur at tapping 0.0401 wt. % (A65C11VS) and 0.0319 wt. % (A65C10VS-Cr) to the final contents of sulphur after vacuum treatment within the range approx. 0.0027 wt. % (A65C11VS) and 0.0023 wt. % (A65C10VS-Cr). It is also evident from the results that average initial contents of sulphur in steel also differ within the range of 0.0082 wt. %. This difference can be explained by use of the charged material (steel charge) with higher contents of sulphur, namely in the heats with the synthetic slag A65C11VS.

![Fig. 2](image_url) Achieved contents of sulphur at individual stages of steel treatment
During the first technological operation consisting of tapping of steel from EAF into ladle (LADLE) the lowest average degree of desulphurisation was achieved (Fig. 1a and Fig. 1b) $\eta_{S\text{LADLE}} \approx$ approx. 23 % for both types of synthetic slags A65C11VS and A65C10VS-Cr. This trend can be explained by insufficient and only beginning dissolving of slag-making additions which are not able to desulphurise intensively [15]. During tapping, significant decrease of steel temperature appears which also makes the conditions of steel desulphurization worse. At tapping of steel from EAF, dosing of slag-making additions (mixture of lime and tested synthetic slags), deoxidation of steel, deactivation of slag and partial alloying of steel happen. At tapping of steel into ladle, sequential stirring and dissolving of individual components appear. That's why at stirring the liquidus temperature of mixture of oxides gradually decreases, till partial or local melting of ladle slag is achieved, which partly participates in desulphurisation of steel in a short time interval lasting from 3.5 to 7 minutes.

It follows from the results (Fig. 1 to Fig. 2), that the main part of desulphurisation of steel took place during treatment of steel in the ladle furnace LF and in the vacuum unit VD. During treatment of steel in the ladle furnace LF a triple increase of the degree of desulphurisation $\eta_{S\text{LF}}$ in comparison with $\eta_{S\text{LADLE}}$ takes place. For the synthetic slag A65C10VS the achieved average degree of desulphurisation $\eta_{S\text{LF}} \approx$ was approx. 66 %, and in the case of the synthetic slag A65C10VS-Cr the average degree of desulphurisation $\eta_{S\text{LF}} \approx$ was approx. 72 % (Fig. 1a and Fig. 1b). Degrees of desulphurisation $\eta_{S\text{LF}}$ achieved different values, but average drop of the contents of sulphur in the steel is on the same level in the range of 0.0207 wt. % ($A65C11VS$) and 0.0202 wt. % ($A65C10VS-Cr$).

 Significant increase of the degree of desulphurisation $\eta_{S\text{LF}}$ and uniform difference in the contents of sulphur in the steel can be explained by dissolution of slag-making additions, by modification of chemical composition of slag by the second dose of slag-making additions together with material for protection of lining, calcium carbide and aluminium in various forms.

It is also possible to state, that higher degree of desulphurisation $\eta_{S\text{LF}}$ of approx. 6 % for the synthetic slag A65C10VS-Cr was caused by lower initial contents of sulphur in the steel at the beginning of steel treatment in the ladle furnace by the heats where synthetic slag A65C10VS-Cr was used.

During the last technological operation presenting treatment of steel in the vacuum unit VD, another significant desulphurisation takes place (Fig. 1 to Fig. 2). In case of the synthetic slag A65C11VS the degree of desulphurisation $\eta_{S\text{VD}} \approx$ was approx. 73 %, and in case of the synthetic slag A65C10VS-Cr the achieved degree of desulphurisation $\eta_{S\text{VD}} \approx$ was approx. 62 % (Fig. 1a and Fig. 1b). The achieved degrees of desulphurisation of steel in both synthetic slags A65C11VS and A65C10VS-Cr can be explained by complete dissolution of slag-making additions, relatively higher temperature of steel and by intensive stirring of steel with the refining slag during the process of vacuum treatment, which has big impact on kinetic conditions of steel desulphurisation.

In case of the synthetic slag A65C10VS-Cr the degree of desulphurisation $\eta_{S\text{VD}}$ decreased approx. by 11 % in comparison with the refining slag with the synthetic slag A65C10VS. This lower degree of desulphurisation was reflected also by lower decrease of the contents of sulphur in the steel. Average value was 0.0051 wt. % ($A65C10VS-Cr$) in comparison with 0.0076 wt. % ($A65C11VS$). This trend can be explained by contents of sulphur in steel that were lower by one third at the start of treatment in the vacuum unit VD at use of the synthetic slag A65C10VS-Cr. The final slag mixture of both types of synthetic slags A65C11VS and A65C10VS-Cr formed in
the course of treatment in the ladle furnace LF and in the vacuum unit VD can be characterised as liquid refining slag, which participates in a significant manner in reactions between slag and metal.

The last part of evaluation of results consists of assessment of influence of synthetic slags A65C11VS and A65C10VS-Cr containing Cr₂O₃ (in the range from 0.3 and 3.0 wt. %) on increase of chromium contents in steel. First, theoretical calculation of the maximal possible capture of chromium from briquetted synthetic slags into steel was made. It should be noted that Cr₂O₃ represents easily reducible oxide and it is therefore possible to assume that it will get reduced (with the element with the highest affinity to oxygen), and steel will be fouled with chromium. Aluminium as the most suitable reduction agent was chosen, which is added in the form of Al ingots (deoxidation agent), and also in the form of Al skimming and Al granular (slag deactivation agent). Theoretically possible maximal reduction will thus take place at reaction with the dissolved aluminium added during tapping of steel into ladle (the first dose of slag-making additions) or in the ladle furnace LF (the second dose of slag-making additions) in accordance with the following equation:

\[(\text{Cr}_2\text{O}_3) + 2\text{Al} \rightarrow (\text{Al}_2\text{O}_3) + 2[\text{Cr}]\]  

By substitution of molar masses of individual components into the equation (1) it is possible to determine from information from the heat records the maximal theoretical contribution of chromium from the synthetic slag A65C11VS or A65C10VS-Cr into steel. In case of the synthetic slag A65C11VS (0.3 wt. % of Cr₂O₃) it is possible to calculate on the basis of the equation (1) with substituted molar masses of individual components, that the average maximal theoretical increase of chromium should be 5 ppm. Using the equation (1) it is possible to calculate for the synthetic slag A65C10VS-Cr (3.0 wt. % of Cr₂O₃), that the average maximal theoretical increase of chromium should be 48 ppm.

![Fig. 3 Achieved contents of chromium during treatment of steel](image)

It is evident from contents of chromium in steel (Fig. 3), that in the heats with the synthetic slag A65C10VS-Cr the average contents in steel after tapping from EAF into ladle was by 249 ppm lower than in heats with the synthetic slag A65C11VS. It is possible to assume that this distinct
difference consists in different (worse) quality of the used steel charge in case of the synthetic slag A65C11VS, which was manifested also by higher initial contents of sulphur in steel than in case of the synthetic slag A65C10VS-Cr. It follows from the achieved results (Fig. 3), that in the heats with the synthetic slag A65C10VS-Cr significant increase of contents of chromium during all technological operations (EAF→LF→VD) appears. The biggest differences in these contents occur from tapping and during transport of the ladle to the ladle furnace, which can be explained by dissolution of ferro-alloys, slag-making additions and deoxidation additions during tapping and by subsequent heating at the beginning of treatment in the ladle furnace LF. The lowest increases in the chromium contents in steel occur in the vacuum unit VD, when during this operation a liquid refining slag is already formed and the main objective consists in reduction of the sulphur contents in steel below 0.005 wt. % and in reduction of gas contents in steel (hydrogen and nitrogen).

It also follows from the results (Fig. 3), that average increase of chromium contents during treatment of steel (EAF→LF→VD) at use of the synthetic slag A65C11VS was 74 ppm, and in case of the synthetic slag A65C10VS-Cr it achieved the average value of 182 ppm. If we deduct from these values the calculated maximal theoretical increases of the chromium contents from the synthetic slag A65C11VS ~ 5 ppm and from the synthetic slag A65C10VS-Cr ~ 48 ppm, we get the average increase of chromium contents in steel from other sources than synthetic slags present. For the heats with the synthetic slag A65C11VS this increase is 69 ppm and for the heats with the synthetic slag A65C10VS-Cr it was 134 ppm.

In case of heats with the synthetic slag A65C10VS-Cr during secondary metallurgy apart from the added synthetic slag also approx. double quantity of chromium is reduced into steel (after deduction of chromium from the synthetic slag) than in the heats with the synthetic slag A65C11VS. Possible sources of chromium may be for example: overflown furnace slag or ferro-alloys containing chromium. Another important source may be also chromium penetrated in the ladle lining from the previous heat alloyed by chromium (e.g. 42CrMo4 or 34CrNiMo6).

It may be also stated that chromium contents in steel in case of both synthetic slags achieved the values of 0.12 wt. % ~ A65C11VS and 0.11 wt. % ~ A65C10VS-Cr, and they are considerably lower than the determined maximal chromium contents at steel St52-3 ~ max. 0.30 wt. %.

Application of synthetic slags A65C11VS and A65C10VS-Cr brought certain increase of chromium contents in steel, but it follows from the results that quality of the used charge had more pronounced influence on the chromium contents in steel.

4 Conclusion

In industrial conditions of the steel-shop at the VHM a.s. a series of experimental heats with use of two types of synthetic slags with focus on evolution of desulphurisation and assessment of influence of oxide Cr₂O₃ on increase of chromium contents in steel was made. On the basis of achieved results of industrial experiments it is possible to define the following findings:

• it is evident from comparison of the resulting degrees of desulphurisation ηs Σ, that at use of both synthetic slags A65C11VS and A65C10VS-Cr a very high degree of steel desulphurisation is achieved, which varies approx. between 91 to 93 %.
• different initial average contents were determined from contents of sulphur in steel in the range of 0.0082 wt. %. This difference can be explained by use of less quality charge material (steel charge) with higher content of sulphur, namely in the heats with the synthetic slag A65C11VS.
• during treatment of steel in the ladle furnace LF and in the vacuum unit VD the main part of desulphurisation of steel took place. This trend can be explained by complete dissolution of the first and second dose of slag-making additions, by modification of chemical composition of ladle slag and by relatively higher temperature.
• after arrival to the ladle furnace, slag in the ladle is modified by the second dose of slag-making additions with the aim of increase of lime contents in the slag, deactivation of slag and heating for dissolution of slag-making additions. In this way, liquid refining slag was created in the ladle furnace.
• it is evident from chromium contents in steel that in the heats with the synthetic slag A65C10VS-Cr the average content in steel after tapping from EAF into the ladle was by 249 ppm lower than in the heats with the synthetic slag A65C11VS. It may be presumed that this significant difference was cause by different (worse) quality of the used steel charge.
• at application of both types of synthetic slags it may be expected that during secondary metallurgy treatment the following maximal theoretical increases of chromium contents in steel may occur: 5 ppm ~ A65C11VS and 48 ppm ~ A65C11VS.
• in the heats with the synthetic slag A65C10VS-Cr approx. double quantity of chromium gets reduced into steel apart from the added synthetic slag (after deduction of chromium from the synthetic slag) than in the heats with the synthetic slag A65C11VS.
• possible sources of chromium (apart from synthetic slags) can be e.g. overflown furnace slag, ferro-alloys, but also furnace lining, which contains chromium from the previous heat (alloyed with chromium, e.g. 42CrMo4 or 34CrNiMo6).
• the achieved chromium contents in steel were in case of both synthetic slags 0.12 wt. % ~ A65C11VS and 0.11 wt. % ~ A65C10VS-Cr, and they are considerably lower than the maximal allowed contents of chromium at steel St52-3 ~ max. 0.30 wt. %.
• our attention in the next stage of research will be focused on confirmation of these industrial results at production of different steel grades with higher contents of chromium at use of the synthetic slag A65C10VS-Cr.

References

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