

## POSSIBILITIES FOR DESULPHURIZATION OF AN ALLOY STEEL IN A VOD DEVICE WHILE USING CHEMICAL HEATING

### MOŽNOST RAZŽVEPLJANJA LEGIRANEGA JEKLA V VOD-NAPRAVI Z IZKORIŠČANJEM KEMIJSKEGA OGREVANJA

Karel Michalek<sup>1</sup>, Libor Čamek<sup>1</sup>, Karel Gryc<sup>1</sup>, Tomáš Huczala<sup>2</sup>,  
Vladimír Troszok<sup>2</sup>

<sup>1</sup>VŠB-Technical University of Ostrava, FMME, Department of Metallurgy and Foundry, 17. listopadu 15/2172, 708 33 Ostrava, Czech Republic

<sup>2</sup>Třinecké železářny, a. s., Průmyslová 1000, 739 70 Třinec-Staré Město, Czech Republic  
karel.michalek@vsb.cz

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The paper describes the knowledge about and results of the experimental heats performed in an electric steel plant. The aim was to verify the possibilities of a controlled desulphurization of alloy steel in a VOD (Vacuum Oxygen Decarburization) device, particularly when using chemical heating through the OVD process (Oxygen Vacuum Deoxidation/Degassing), as well as the standard slag formers. Experimental procedures were used in the production of alloy tool steel. Both, the system of making the reducing slag and optimizing the composition of individual oxides in order to achieve the desired basicity, are complicated by the products of the chemical heating. Therefore, it was necessary to develop a new production technology that would eliminate such oxide products of chemical heating and, thus, the maximum degree of desulphurization could be achieved. The main principle of the technology is to create appropriate thermodynamic and kinetic conditions required for desulphurization. In particular, this concerns a low oxygen activity in the steel, the composition of refining slag, and an intense bath stirring with argon.

Keywords: steel desulphurization, VOD device, OVD process, slag, steel cleanliness

Članek opisuje znanje in rezultate raziskave eksperimentalnih talin, izdelanih v elektrojeklarni. Namen je bil preveriti možnost kontroliranega razžvepljanja legiranega jekla v VOD (Vacuum Oxygen Decarburization)-napravi, posebno med uporabo kemijskega ogrevanja med OVD (Oxygen Vacuum Deoxidation/Degassing)-postopkom, kot tudi standardnih gradnikov žlindre. Eksperimentalni postopki so bili uporabljeni pri proizvodnji legiranega orodnega jekla. Oboje, tvorba reduktivne žlindre in optimalna sestava posameznih vključkov, z namenom doseganja zelene bazičnosti, ovirajo produkti kemijskega ogrevanja. Zato je bilo potrebno razviti novo tehnologijo proizvodnje, ki bi preprečila oksidne produkte kemijskega ogrevanja, kar bi omogočilo doseganje maksimalne stopnje razžvepljanja. Osnovni princip nove tehnologije je zagotoviti ustrezne termodinamične in kinetične pogoje, potrebne za razžvepljanje. To pomeni nizko aktivnost kisika v jeklu, sestavo rafinacijske žlindre in intenzivno mešanje kopeli z argonom.

Ključne besede: razžvepljanje jekla, VOD-naprava, OVD-postopek, žlindra, čistost jekla

## 1 INTRODUCTION

The technology of the production of alloy tool steels require a special preparation of the input materials, followed by a strict compliance with technological and metallurgical processes when producing steel in a 10-ton electric arc furnace (EAF), as well as the ladle's optimal preparation. The final steel processing in a VOD device requires a continuous and systematic management of individual production stages, in particular the chemical heating, creating a high vacuum, production of reduction and refining slag<sup>1,2</sup>, additional steel alloying, and continuous, optimal purification with argon.

The required steel desulphurization in the VOD device can only be achieved by mastering the technology and metallurgy of the processes, especially by optimizing the slag regime and complying with the basic thermodynamic and kinetic conditions of a desulphurization reaction.

## 2 PRINCIPAL FACTORS AFFECTING THE REQUIRED DEGREE OF STEEL DESULPHURIZATION

In the paper formerly presented<sup>3</sup>, the technology of the low-sulphur-content steel production (up to the mass fraction  $w = 0.002$  %) in the conditions of EAF using CaO and Refraflux additives was described in detail. With regard to the product range of tool steels, desulphurization technology in the VOD device with an oxidation stage at the beginning of the process, used for the chemical heating of steel, has been assessed and gradually developed.

The desired degree of desulphurization in a vacuum station when applying chemical heating is largely limited by the output sulphur content from EAF. In the production of alloy steel grades in VOD, the chemical-heating method creates entirely different starting conditions for the formation of the reducing slag compared to the standard technological processes in EAF. Nevertheless,



(OVD) in the production of the alloy tool-steel grade 19569 (X63CrMoV5.1). **Table 1** shows the internal release chemical composition of the steel grade 19569.

**Table 1:** Internal release chemical composition of 19569 steel in mass fractions, w/%

**Tabela 1:** Interna kemijska sestava jekla 19569 v masnih deležih, w/%

Chemical composition	19569 (X63CrMoV5.1) w/%
C	0.58–0.68
Si	0.7–1.1
Mn	0.25–0.55
P	max. 0.015
S	max. 0.010
Cr	4.5–5.5
Mo	0.8–1.2
V	0.2–0.4
W	max. 0.6

The output from EAF is the sulphur content of  $w = 0.005\%$  achieved as a standard, which can be, during the subsequent processing with the VOD technology using chemical heating, maintained at the achieved level or reduced below the given limit.

The technological process involved the following operations:

- Dislodging the reducing slag from the ladle after tapping EAF. This part of the technology is, from the perspective of preventing the reverse transition of sulphur from the slag into the metal and the possibility of creating a new reducing slag, very favourable. However, it also negatively affects the heat loss through the uncovered steel surface, which increases the need for the strength of the chemical heating.
- A creation of a new cover slag on the steel surface. This was carried out by applying the basic charge of 50 kg lime and by adding again the same charge of lime in addition to an approximately 20 kg of fluorite upon the installation of the casting ladle (CL) into the VOD device.
- An addition of aluminium and oxygen-blowing in one or two stages combined with chemical heating, in this way the temperature was increased by 150–200 °C above the liquidus temperature of the alloy steel grade produced.
- A gradual formation of a non-foaming reducing slag caused by the lime additive.

- Steel evacuation to perform a vacuum deoxidation and to create conditions for increasing the cleanliness of the steel including its precise additional alloying.
- Temperature and chemical homogenization with argon at atmospheric pressure, whose duration was set by the temperature margin of the gradual, controlled cooling, within which the treatment of the chemical composition of the reducing slag was carried out, or small corrections to the chemical composition of the alloy tool steel were made.
- After reaching the required steel temperature above the liquidus, the processing in VOD was completed and the casting into the moulds was done.

In the process of gradual cooling from the temperatures after the chemical heating, it was difficult to approach the optimum values of the chemical composition of the reducing slag, which should contain mass fractions from 45 % to 55 % CaO, 18 % to 25 % Al<sub>2</sub>O<sub>3</sub>, ≤ 10 % SiO<sub>2</sub>. At the same time and in accordance with the theory of steel desulphurization, it was also very important to maintain a low oxygen activity in the metal. This requirement has been, in terms of the VOD device, met particularly by maintaining the maximum possible content of aluminium in the liquid metal. Suitable kinetic conditions were continuously provided with the optimum control – blowing argon through the bottom porous block with the volumetric flow rates of up to 20 l min<sup>-1</sup>.

## 5 ACHIEVED RESULTS

The course of each experimental heat was, in the secondary metallurgy VOD with chemical heating, to some extent, unique. A total of 10 heats were produced. The aim was to verify the options of the controlled steel desulphurization in the VOD device using chemical heating (OVD) as well as the standard slag-forming additives. The comparison of the basic chemical analyses of the slag and steel of the selected 19569 heat grade tested is shown in **Table 2**.

The achieved results describing the composition of the final reducing slag after the steel processing show some differences, especially the differences for Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> oxides. These variations result from individual processing procedures in the VOD device in relation to the method of how to control chemical heating. In most of the heats the CaO/Al<sub>2</sub>O<sub>3</sub> ratio ranged from 1.0 to 2.63, and the basicity (CaO/SiO<sub>2</sub>) was in the range from 2.15 to 10.

**Table 2:** Selected chemical analyses of the final reducing slag and steel grade 19569 in mass fractions, w/%

**Tabela 2:** Izbrane kemijske analize končne redukcijske žilindre jekla 19569 v masnih deležih, w/%

Heat No.	CaO	Al <sub>2</sub> O <sub>3</sub>	MgO	SiO <sub>2</sub>	FeO	Cr <sub>2</sub> O <sub>3</sub>	MnO	S <sub>steel</sub>	Temperature before chemical heating	Temperature after chemical heating
4	35.49	35.82	2.74	13.22	0.35	0.19	0.17	0.0030	1559 °C	1682 °C
9	40.62	26.38	3.46	18.88	1.03	0.66	0.74	0.0030	1529 °C	1685 °C
6	41.00	31.70	5.20	13.90	0.19	0.32	0.45	0.0030	1544 °C	1723 °C
7	48.37	18.40	4.40	4.80	0.28	0.09	0.01	0.0020	1575 °C	1734 °C

In terms of a successful desulphurization it was very important to maintain the parameters of the input chemical analyses and to optimize the steel temperatures before and after the chemical heating in the VOD device so that the composition of the arising reducing slag was not subsequently tasked, in particular by a high content of aluminium oxide.

During the subsequent processing following the chemical heating it was necessary to continue the adding of lime and, based on the visual inspection results, to substitute the additive for its liquefaction. Based on the information obtained from the chemical analysis, it was recommended to only alloy the materials that do not allow batching the VOD device during the next phase of vacuuming.

The changes in the chemical compositions of the steel and the slag during the processing in the secondary-metallurgy VOD device are shown in **Figures 2** to **5**.

In terms of reducing the slag formation, any deviation from the recommended technology causes deflection from its optimum composition, which prevents the alloy steel from achieving the required degree of desulphurization.

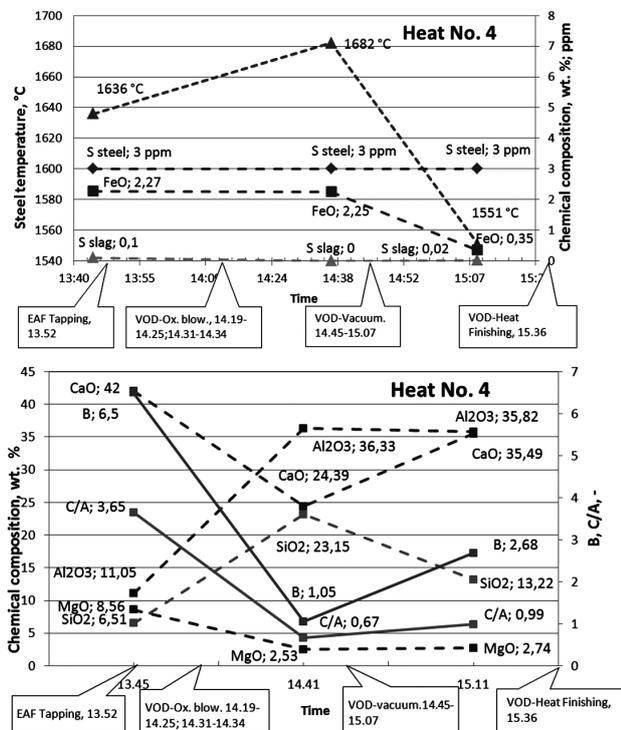
The processing of the No. 4 heat can be shown as an example (**Figure 2**). A low content of CaO in the reducing slag did not ensure a further desulphurization of

the steel, so that the resulting sulphur content was identical to the initial content (30 µg/g).

A similar course of processing can be noted in the cast No. 9 (**Figure 3**), which resulted in a relatively rapid drop in the temperature (due to the insufficient heat capacity of the ladle) following the completion of the vacuuming phase, leading to an unsatisfactory content of CaO in the reducing slag due to the worsened assimilation of lime. The final sulphur content of the heat was identical to the initial content (30 µg/g).

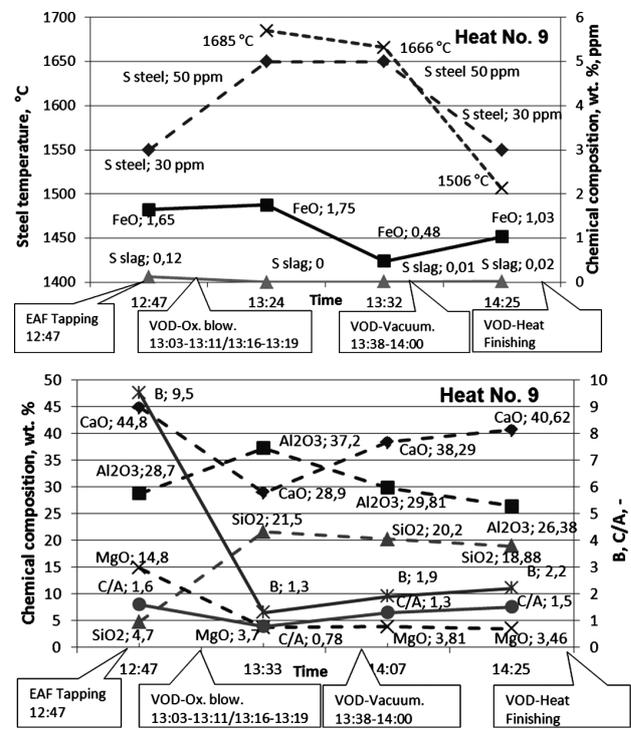
From the course of processing the heat No. 6 (**Figure 4**), where the input sulphur content was 40 µg/g – it is clear that after the completion of the vacuuming phase the sulphur content was increased to 70 µg/g. The result of the repeated measurement of the oxygen activity in the steel showed a higher value (7.3 µg/g), which was probably associated with a low total aluminium content in the steel ( $w = 0.001 \%$ ). The subsequent additional deoxidation by aluminium in the phase of the controlled additional cooling decreased this activity (to 1.7 µg/g), but, on the other hand, it shifted the optimum composition of the reducing slag (too high a content of  $Al_2O_3$ ). Through specified treatments we managed to keep the resulting sulphur content at the value of 30 µg/g.

The process of operating the experimental heat No. 7, whose course is shown in **Figure 5**, has been found to be



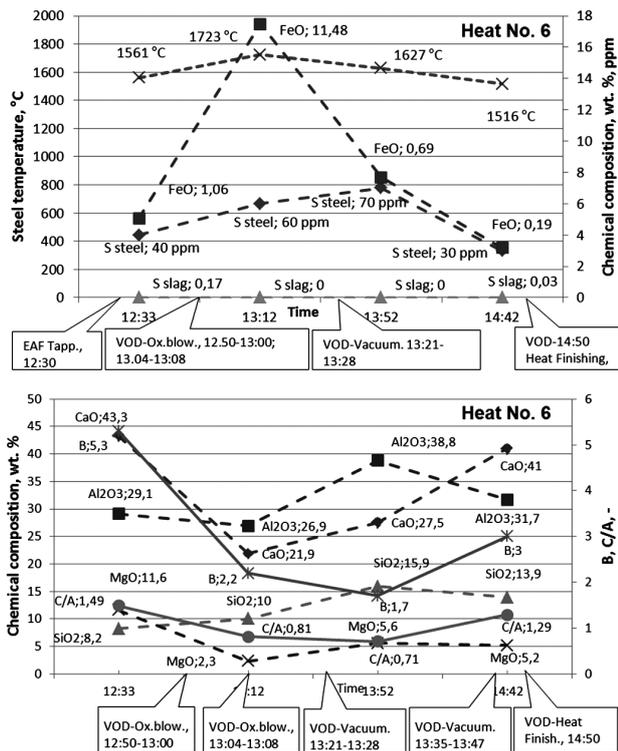
**Figure 2:** Development of the chemical composition of the steel and the slag during the secondary-metallurgy processing in the VOD device with chemical heating in the heat No. 4

**Slika 2:** Razvoj kemijske sestave jekla in žlindre med procesom sekundarne metalurgije v VOD-napravi s kemijskim segrevanjem taline št. 4



**Figure 3:** Development of the chemical composition of the steel and the slag during the processing in the secondary-metallurgy VOD device with chemical heating in the heat No. 9

**Slika 3:** Razvoj kemijske sestave jekla in žlindre med procesom sekundarne metalurgije v VOD-napravi s kemijskim segrevanjem taline št. 9

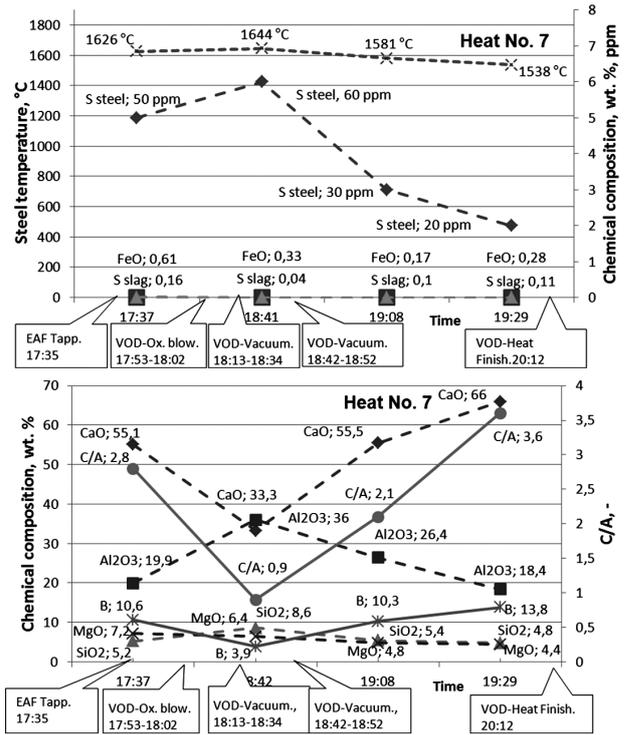


**Figure 4:** Development of the chemical composition of the steel and the slag during the processing in the secondary-metallurgy VOD device with chemical heating in the heat No. 6  
**Slika 4:** Razvoj kemijske sestave jekla in žlindre med procesom sekundarne metalurgije v VOD-napravi s kemijskim segrevanjem taline št. 6

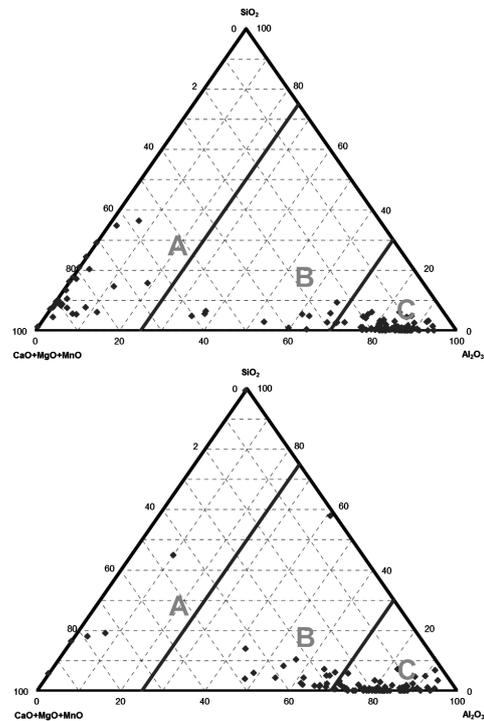
the optimal course of the steel processing in the secondary-metallurgy VOD device with chemical heating. The initial sulphur content in the steel of 50 µg/g was, after meeting the recommended procedures for the steel-processing technology, reduced to the resulting content of 20 µg/g. What contributed to this result were not only a suitable composition of the reducing slag (CaO > 50 %, B > 5, CaO/Al<sub>2</sub>O<sub>3</sub> > 2, FeO < 0.3 %), and a low oxygen activity in the steel (1.4 µg/g), but also the stirring of the steel.

### 6 IMPACT OF TECHNOLOGY ON CLEANLINESS OF STEEL

The carried-out experimental heats were assessed in terms of the achieved cleanliness of the steel. An electron microanalyzer Hitachi S-3500N was used for the evaluation, on the basis of which we determined the framework compositions of non-metallic inclusions, their numbers and geometrical proportions. The achieved results for the heats No. 6 and No. 7 are shown as the ternary diagrams in Figure 6. As for these heats, the lime additive was, in the final phase of the controlled additional cooling, added with no fluorite additive. This led to a cooling of the reducing slag, increasing its viscosity, and a worsening of the kinetic conditions for



**Figure 5:** Development of the chemical composition of the steel and the slag processing in the secondary-metallurgy VOD-device with chemical heating in the heat No. 7  
**Slika 5:** Razvoj kemijske sestave jekla in žlindre med procesom sekundarne metalurgije v VOD-napravi s kemijskim segrevanjem taline št. 7



**Figure 6:** Ternary diagrams as a result of the chemical microanalysis of the inclusions from the heats No. 6 and No. 7  
**Slika 6:** Ternarni diagrami kot rezultat kemijske mikroanalize vključkov iz talin št. 6 in št. 7

the absorption of non-metallic inclusions, which also led to a higher incidence of the inclusions based on CaO-Al<sub>2</sub>O<sub>3</sub>. The micro-purity results for the other experimental heats were standard.

## 7 CONCLUSION

The production technology of the controlled steel desulphurization with a requirement to keep the target sulphur content below 0.0050 % was optimized in the VOD device using chemical heating of the steel. Technologies have been applied in the production of the alloy tool-steel grade No. 19569 (X63CrMoV5.1). The main issue in the design of the technology was that the systems for the production of the reducing slag and optimized compositions of individual oxides have been disrupted by the chemical-heating products.

The essential problems are the amount of Al<sub>2</sub>O<sub>3</sub>, which is formed after the chemical heating during the oxidation of added aluminium by gaseous oxygen and, simultaneously, the formed quantity of the easily reducible oxides MnO, FeO and Cr<sub>2</sub>O<sub>3</sub>. With regard to this, it is necessary to add high quantities of CaO to achieve an appropriate content of free CaO and an increase in the CaO/Al<sub>2</sub>O<sub>3</sub> ratio. However, this quantity results in a noticeable drop in the temperature during the heat completion. The reduction of oxides is completed after the vacuuming.

In accordance with the theory of steel desulphurization, the efficiency of maintaining a low oxygen activity in the metal where the FeO content in the slag is below 1 % was confirmed. This requirement has been ensured in the VOD device after the chemical heating primarily by maintaining the maximum possible aluminium content in the liquid metal. It is also necessary to maintain the appropriate slag basicity (over

5) and the CaO/Al<sub>2</sub>O<sub>3</sub> ratio, which should be in the range of 1.8 to 2.2.

Results of the microanalysis of the inclusions showed that, to achieve the desired cleanliness of the tested steel grade, it is required, after the completed vacuuming, to run the final phase of processing the reducing slag only with the optimum steel temperature, weight and chemical composition of the slag. It was found that an increase in the CaO additive changes the chemical compositions of the inclusions, in particular causing an increase in the CaO content. The impact of the change in the chemical compositions of the inclusions on the beneficial properties of the steel will be monitored with a final customer.

## Acknowledgements

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