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**Oxygen distribution between phases during ladle processing of
 aluminum killed bof steels**

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**Розподіл кисню між фазами при ковшовій обробці
 алюмінієвих сплавів**

The modern state of secondary metallurgy is characterized by the sustainable development of technologies that ensure high metal quality by reducing the number of non-metallic inclusions, the which is closely related to the oxygen content in steel after smelting. Therefore, the issues of regularities of oxygen distribution between phases at the stage, BOF - CCM.

Purpose. The aim of the research was to determine the conditions of redistribution of oxygen dissolved in the metal depending on the stages of steel processing, to determine the degree of approach of deoxidation processes to thermodynamic equilibrium.

Methodology. Research was carried out in industrial scale. Steel grades 34Cr and 36CrB were smelted in BOF of 170-t capacity. Processing of crude steel was carried out in a LF unit with further vacuum degassing and without it and transfer of steel to CCM. At each stage of steel treatment, metal and slag samples were taken using an automatic sampler to determine the chemical composition, and the temperature. Oxygen content were monitored using a "Celox" analyzer. Findings. The carried-out studies showed that before the end of metal processing in the ladle, it is possible to detect individual reoxidation processes caused by unwanted ingress of oxygen from the air and from ladle slag oxides. According to calculations, in the second half of processing in the ladle and during casting, there is a slight deoxidation of steel with aluminum due to a decrease in temperature. Even if during this time due to the exchange reaction between steel and slag, a small amount of Mn and Si is recovered from the ladle slag, while its composition is practically constant throughout the period of steel processing in the ladle, while the metallurgical reactions proceed in the region of thermodynamic equilibrium.

Originality. It has been determined that oxygen activity in steel varies unevenly over time and decreases to 3 ppm by the end of treatment in the ladle. While in each case it is in the Fe – a[O] – Al system near the calculated values of thermodynamic equilibrium.

Practical value. The use of the obtained regularities makes it possible to obtain the specified content of aluminum in steel for the studied assortment and to predict the burning of deoxidizers and alloying elements, ensuring the reliability of obtaining the required chemical composition of steel with a high degree of purity.

Key words: reoxidation, deoxidation, oxygen activity, slag, metal, non-metallic inclusion

After blowing end in the converter, the oxygen activity in steel is in the range of 1000-1500 ppm [1-3]. After tapping from the vessel to a teeming ladle, the oxygen content in the metal is reduced by secondary metallurgy processes in order to provide high-quality of continuously cast billets and high purity of steel. At this stage steel reaches necessary temperature and chemical composition.

Important for theory and practice are patterns of oxygen distribution between phases at each stage of secondary metallurgy, studied directly under production conditions. This distribution determines the removal efficiency of harmful impurities, non-metallic inclusions and gases from the steel. It is advisable to compare the measured oxygen contents with equilibrium states, which can be easily achievable in practice, and their calculation can be carried by metallurgical scientists.

Ladle slag

The metallurgical efficiency of the ladle slag is enhanced by bubbling of the ladle content with neutral gases, since the reactions are accelerated by increasing the specific surface of the interacting phases, delivering reagents to the reaction zone for a short period of time.

Depending on the customer's requirements for the content of harmful impurities in steel, slag of the 1st (better) or 2nd grade (cheaper) is formed in the ladle by adding the appropriate materials when the steel is blown with argon Table 1.

Table 1. Chemical composition of ladle slags of secondary metallurgy

Grade, % wt.	CaO	Al ₂ O ₃	SiO ₂	MgO	FeO + MnO
1	50-58	30-35	5-6	5-7	< 1, 0
2	50-58	21-26	10-15	8-10	< 1, 0

Steel deoxidation

A decrease in the oxygen content in steel can be achieved in two ways: 1) diffusion deoxidation by forming slag with a high possibility of oxygen absorp-

tion and, due to falling temperature and/or 2) precipitating deoxidation, by adding elements that have a high affinity for oxygen [4]. The elements C, Mn, Si,

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and Al in the presented sequence have a higher affinity for oxygen than iron. With decreasing temperature, the oxidation capabilities of Si, Mn, and Al increase due to the formation of solid or liquid deoxidation products. On the contrary, carbon deoxidation due to the formation of gaseous products of CO and CO₂ has its own characteristics. The influence of carbon in the deoxidation process increases under vacuum and/or with increasing temperature so that at temperatures above 1600 °C and a partial pressure of 10⁻³ MPa, carbon is a stronger deoxidant than Al. When analyzing the equilibrium state, it should be taken into account that the deoxidants and oxygen are in liquid steel in dissolved form. For this reason, the calculations should take into account the reagents activity in the reactions and the heat of release of products [5]. The process of deoxidation does not end with the addition of deoxidizing elements: with a decrease in temperature, further deoxidation products are constantly formed, which can be different depending on the time of their appearance. The maximum possible oxygen content in pure iron lies between 1860-2800 ppm in the temperature range 1530 and 1700 °C. The effect of the C, Si, Mn, and Al on the oxygen content in steel is calculated by the interaction parameters determined in [6].

Deoxidant Burnout

C, Si, Mn, and Al react with oxygen dissolved in steel. The formed oxides are removed from the metal to the slag, and all but CO are absorbed by the slag. The high oxygen content in steel, the significant specific surface area of the "fluffy" metal stream when the

melt is tapped from the converter, and therefore the possibility of oxygen absorption from the ambient air, as well as the ingress of converter slag into the ladle, increase the burning of alloying and deoxidant materials.

The primary goal should be to monitor in production conditions the behavior of oxygen dissolved in steel at each of the stages of secondary metallurgy, to determine the level of approximation of deoxidation processes to thermodynamic equilibrium.

Materials and methods of research

The experiments have been carried out at the plant "A" in converters of 170-t capacity on melts analytically close steel grades 34Cr and 36CrB with vacuum degassing and without it. As slag-forming materials, varying amounts of lime (with a CaO content of at least 95%) and calcium aluminate (25% CaO and 75% Al₂O₃) have been used. During steel tapping from the converter and each 10-15 minutes after that metal and slag samples using an automatic device were taken, and the temperature and total oxygen content in steel [O_Σ] were analyzed with a Celox analyzer from Electro-Nite. Slag compositions have been changed according to the program illustrated in Fig. 1, in order to analyze steel deoxidation during metal processing with slag, the compositions of which are ranged between compositions of the 1st and 2nd grade. Changed the ratio of CaO:Al₂O₃:SiO₂ for using cheaper slag-forming materials by increasing the content of SiO₂ (instead of part of Al₂O₃) and maintaining their compliance only with basic requirements.

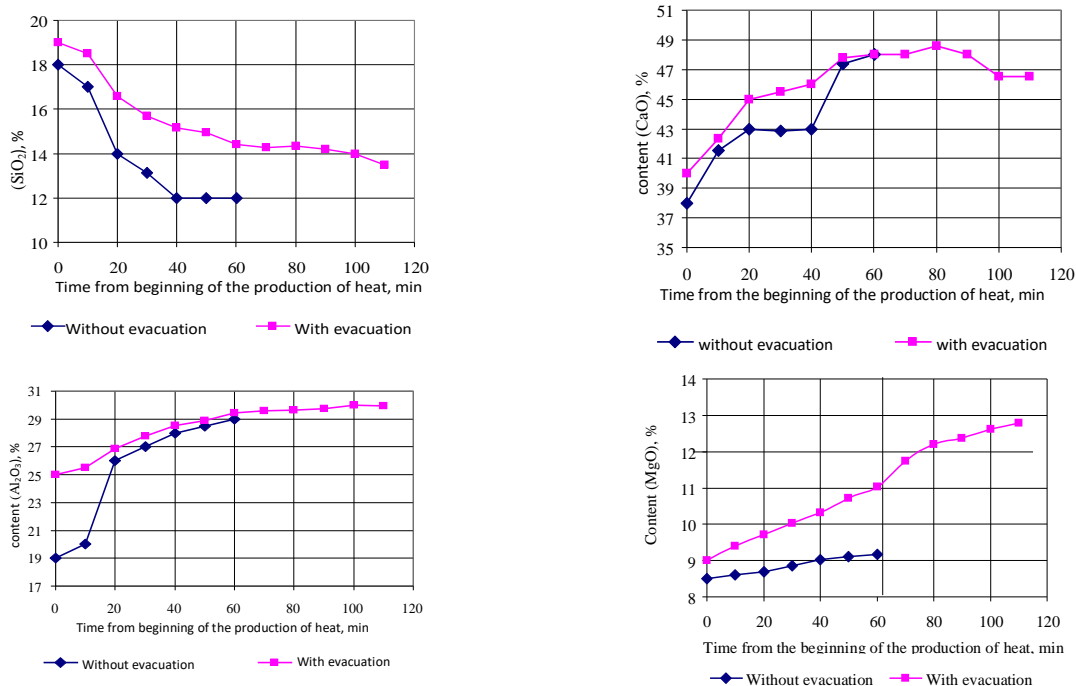


Figure 1 – Change in the composition of the slag during secondary metallurgy processes

Results and discussion

The melt temperature decreases during tapping and steel processing in the ladle from 1650 °C until

the stationary state in the tundish is reached at 1530 °C for melts without vacuum treatment and from 1700 °C to 1570 °C for melts with vacuum treatment. The

average processing time in the ladle from tapping to the start of casting without vacuum treatment is approximately 70 minutes, and 100 min. with vacuum treatment. A 30-minute longer vacuum treatment without heating the steel requires about 50 °C higher tapping temperature.

The concentration of CaO in ladle slag during steel processing was kept at around 50%. The ladle slag

composition of the studied melts was maintained in the CaO:Al₂O₃:SiO₂ system in a state of saturation of CaO and Helenithe (Fig. 2), which determines their high refining and deoxidizing properties [1].

Significant impact on the studied processes of secondary metallurgy has the aluminum content in steel. Prior to addition of calcium cored wire the desulfurization reaction proceeds as follows:

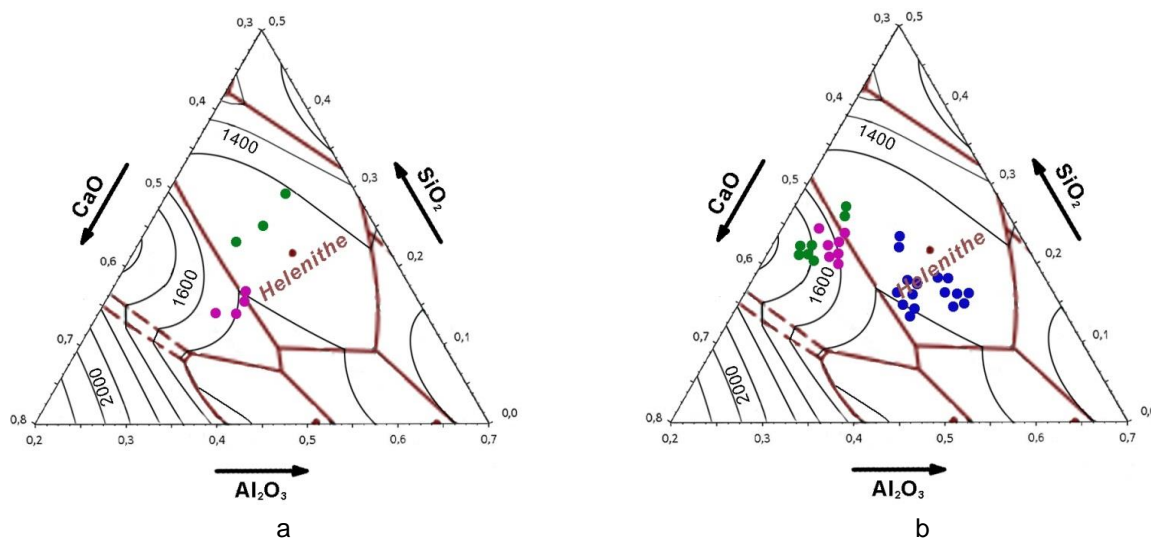
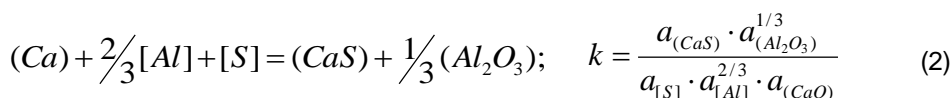
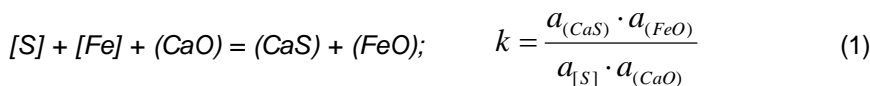


Figure 2 – Three-component diagram of the CaO-Al₂O₃-SiO₂ system

Equations (1) and (2) emphasize that the best desulfurization conditions are created when slag based on calcium aluminates, saturated with CaO, is formed in the ladle (see Fig. 1)

The effect of aluminum is especially high for its contents up to 300-400 ppm, when it acts not only as a desulfurizer, but also as a strong deoxidant that reacts with oxygen dissolved in steel. This is because calcium has a greater chemical affinity for oxygen than sulfur, and interacts mainly with oxygen, and not with sulfur. Moreover, in an oxidized metal, surface-active oxygen occupies part of the surface, lowering the content (chemical activity) of the same surface-active sulfur in the surface layer, where desulfuration processes develop. Only with a significant decrease in the oxygen content in steel less than 10 ppm during deep deoxidation, the calcium addition would become effective. Therefore, calcium was added into steel as a part of cored wire with a consumption of 0.24-0.25 kg/t of steel after deep deoxidation with aluminum. The following circumstance is also important. The probability of non-metallic inclusions adsorption to argon bubbles increases with increasing interfacial tension at their interface with the metal. Since among the

oxide inclusions in steel, the highest interfacial tension has solid alumina (α-Al₂O₃ or corundum), it is most intensively removed by blowing. Since most of the remaining oxygen in aluminum-killed steel is in the form of alumina, during argon blowing the total oxygen content [O]_Σ (dissolved [O]_{dis} and in inclusions [O]_{ox}) decreases.

The aluminum content in steel after tapping was increased to 270 ppm by alloying with aluminum (Fig. 3). During processing in the ladle, the aluminum content decreases due to the deoxidation in decreasing temperature and reoxidation: for melts without vacuum treatment, up to 255-260 ppm; for melts with vacuum treatment up to 220-230 ppm.

As mentioned earlier, the content of active oxygen in steel is also an important characteristic of the steel processing in the ladle. It characterizes (FeO) content in the slag, and also allows to predict the burning of deoxidant, ensuring the accuracy of steel chemical composition (Fig. 4,5).

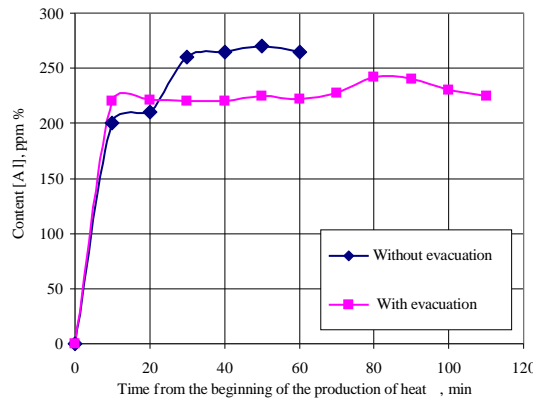


Figure 3 – Change of the aluminum content in the steel

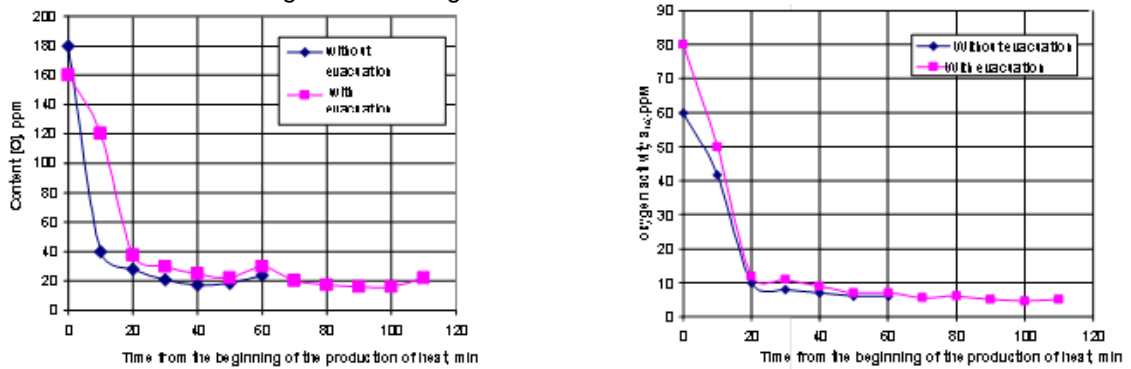


Figure 4 – Changes in the content and activity of oxygen in steel

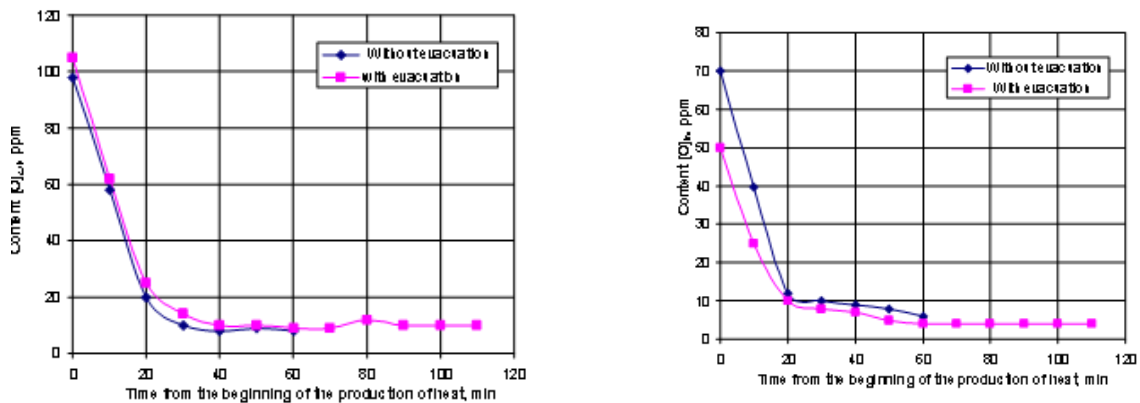


Figure 5 – Change in the content of dissolved and oxide oxygen in steel

The active oxygen content in the steel $[O]_{dis}$ and the total oxygen content $[O]_{\Sigma}$ allows us to judge the content of inclusions $[O]_{ox}$ in the steel, which makes it possible to control the process of their removal:

$$[O]_{ox} = [O]_{\Sigma} - [O]_{dis} \quad (3)$$

$$a_{[O]} = f_{[O]} \cdot [\%O]_{sol} \text{ at } \log f_{[O]} = \sum_{i=1}^n e_{[O]}^i \cdot [\%i] \quad (4)$$

It is proportional to the activity of oxygen:

$$[O]_{sol} = \frac{a_{[O]}}{10^{([\%C] \cdot e_O^C + [\%Si] \cdot e_O^{Si} + [\%Mn] \cdot e_O^{Mn} + [\%Cr] \cdot e_O^{Cr} + [\%Al] \cdot e_O^{Al} + [\%Ca] \cdot e_O^{Ca} + [\%O] \cdot e_O^O)}} \quad (5)$$

After tapping the ladle was moved to a blowing stand, where the metal was intensively blown with ar-

The amount of oxygen dissolved in steel was calculated according to its activity and activity coefficient $f_{[O]}$ using interaction parameters:

gon (Ar) with a flow rate of up to $0.006 \text{ nm}^3/(\text{min} \cdot \text{t})$ for 15-20 minutes, and then switched to the “clean” refin-

ing blowing mode, necessarily covered with slag, for at least 20 minutes with a flow rate 0.009-0.012 nm³/min·t (to refine steel from non-metallic inclusions). After the start of argon blowing total oxygen content in the metal [O]_Σ of all melts were at about 130 ppm. During the steel processing, a constant decrease in [O]_Σ was noted in the ladle. By the beginning of the “clean” blowing, this value was 20 ppm for melts without vacuum treatment and 15 ppm for melts with vacuum treatment. However, during a clean purge, an increase in [O]_Σ was observed in some melts, which indicates that it was not possible to exclude undesirable processes of metal reoxidation.

The oxygen activity in steel decreases during processing from 75 to 3 ppm. The content of dissolved oxygen after tapping was much higher, namely 110 ppm, due to the presence of C, Si, Mn in it. Subsequently, as a result of aluminum deoxidation and a temperature decrease, the [O]_{dis} decreases to 10-15 ppm at the end of the “clean” blowing.

The oxygen content in the [O]_{ox} oxides varies from 10 ppm to a very low level at the end of the “clean” blowing (Fig. 6). Ca in the cored wire was added after deoxidation and vacuum treatment and before “clean” blowing (to refine steel from non-metallic inclusions).

In research, content of [Al], [O]_Σ, [O]_{dis} and (CaO) are provided at theoretically substantiated levels, the aimed results of steel processing have been achieved and are representative of the calculations of thermodynamic equilibrium.

The equilibrium state in the system Fe – a_[O] – Al for respective temperatures are calculated with using data from work [1]. The curves of the dependences of a_[O] on [Al] with decreasing temperature move toward lower contents of aluminum and oxygen in the metal. The a_[O] values we determined as characteristics of the content of chemically dissolved oxygen are close to the corresponding equilibrium values and decrease from 80 ppm after the start of gas purging to 3 ppm at the end of steel treatment in the ladle.

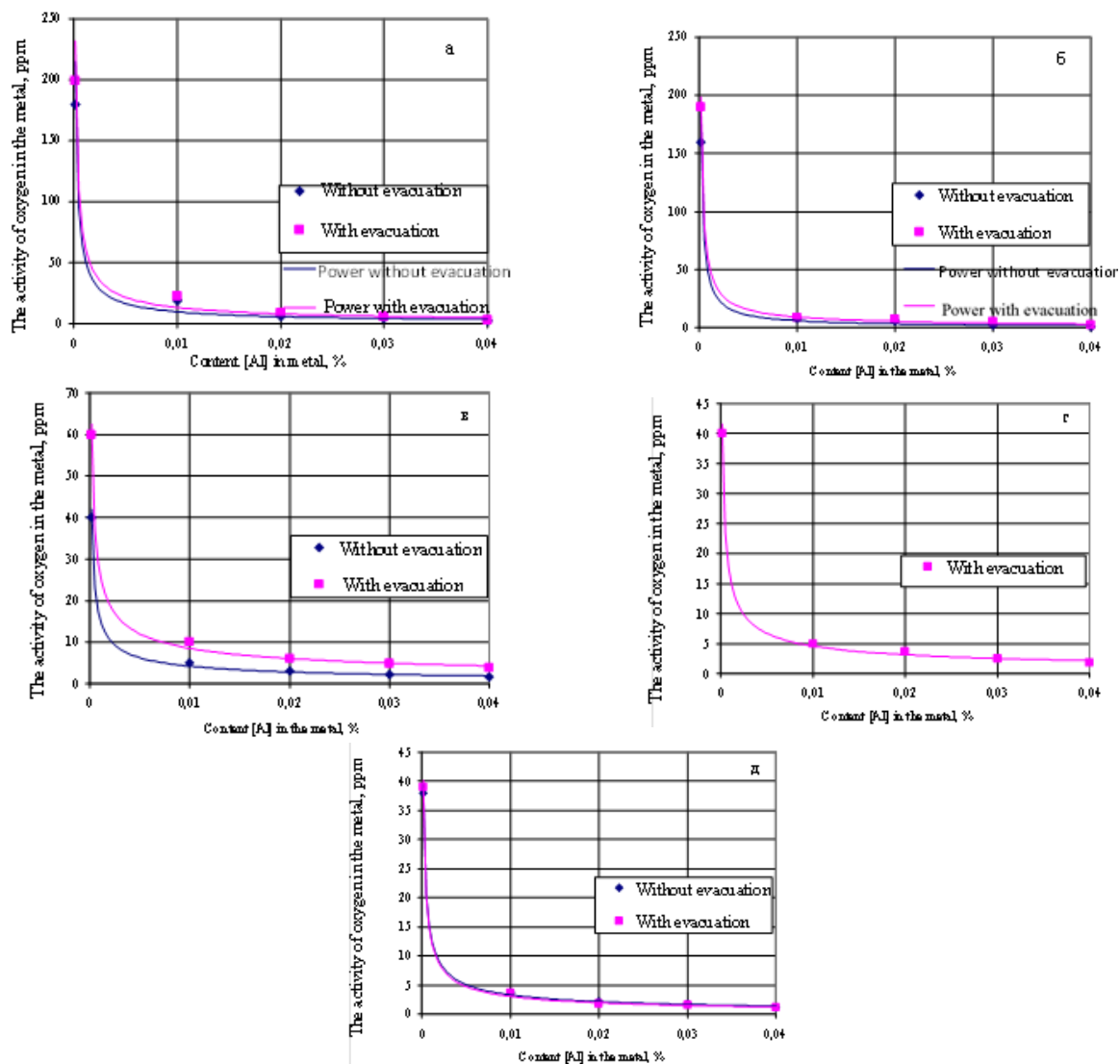
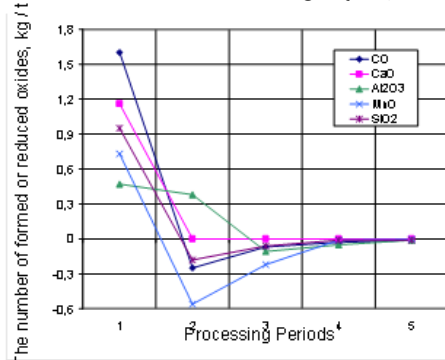


Figure 6 – Change in oxygen activity depending on the aluminum concentration in steel during the ladle treatment (a – the beginning of the purge of Ar; b – before the Ca treatment; c – after the Ca treatment; d – vacuum treatment; e - “clean” argon blowing)

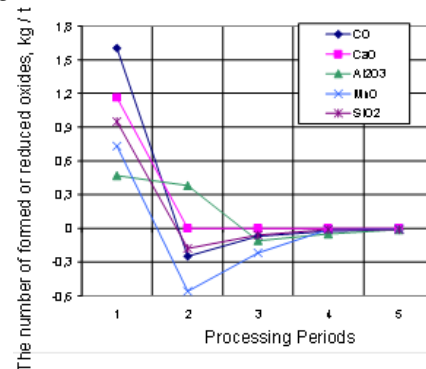
Oxidation of deoxidant

The oxidation of C, Si, Mn and Al per tone of steel is defined depending on the time and for various variants of experiment within the developed program (Fig. 7) Total is the sum of the formed amounts of {CO}, (SiO₂), (MnO), (CaO) and (Al₂O₃) at the corresponding time. Oxidation, regardless of the variant of experiment, occurs most intensively in the first 10 min. after tapping, it reaches 4,91 kg/t for melts without vacuum treatment and 3.62 kg/t for vacuum treated ones. It leads to formation of 1.2-1.7 kg/t {CO}; 0,65-0,78 kg/t



1 – 10 minutes after tapping; 2 – blowing in the ladle; 3 – after refining blowing; 4 – 30 min. tundish; 5 – 60 min. tundish

(SiO₂); 0,07-0,13 kg/t (MnO); 0,7-1,2 kg/t (CaO) and 0,61-0,68 kg/t (Al₂O₃). During further processing of steel in the ladle and casting in the CCM tundish, some oxidation of aluminum was detected, caused by further deoxidation of the metal due to a temperature drop or reoxidation processes. A slight increase in the manganese and silicon content in steel due to their reduction from ladle slag, primarily in melts without vacuum treatment, was found. The decrease of [O]_Σ is 2.4 kg/t for melts without vacuum treatment and 2.1 kg/t for melts with vacuum treatment.



1 – 10 minutes after tapping; 2 – vacuum treatment; 3 – after refining blowing 4 – 30 min. tundish; 5 – 60 min. tundish

Figure 7 – Specific weight of the oxide formed during the ladle treatment (a – without vacuum treatment; b – with vacuum treatment)

Summary

The oxygen content in the metal of the studied melts during the processes of secondary metallurgy is continuously reduced from 130 to 15-20 ppm. By analyzing oxygen behavior before the end of processing in the ladle, one can find single reoxidation processes caused by undesirable access of air oxygen or from ladle slag oxides. The oxygen activity in the steel is 80 ppm after tapping from the converter and decreases by the end of processing in the ladle to 3 ppm. In each case, it is located in the system Fe – a_[O] – Al near the calculated thermodynamic equilibrium.

The most intense oxidation of C, Si, Mn, and Al is observed after the addition of alloying elements during the first 10 min. after the tapping. According to

calculations, in the second half of the processing in the ladle and during casting, there is a slight deoxidation of steel with aluminum due to a temperature drop. Even if a small amount of Mn and Si from the ladle slag is reduced during this period of time due to the exchange between steel and slag, its composition remains almost constant throughout the processing of steel in the ladle, while metallurgical reactions proceed in the thermodynamic equilibrium.

Using the obtained models allows us to obtain an aimed aluminum content in steel (in this study 200 ppm) and to predict the burnout of deoxidizers and alloying elements, ensuring the reliability of obtaining the required chemical composition.

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