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Role of slag in the steel refining process in the ladle

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Properties

ABSTRACT

Purpose: The purpose of this research is to analyse the steel refining technology in a ladle furnace including refining slag formation in the ladle. The research was conducted using chromium-nickel- molybdenum steel intended for heat treatment in order to produce crankshafts.

Design/methodology/approach: This research was conducted in a ladle furnace with the capacity of 65 Mg of steel. Data from 10 melts were analysed. Samples of refining slag and metal were taken to analyse their chemical composition. On their basis researchers analysed the process of desulphurisation of steel at the ladle furnace workstation. Calculations were made concerning the equilibrium chemical composition of slag to determine the share of gas phase, liquid phase and solid precipitations. The calculations were made using a thermodynamic software FactSage 6.2.

Findings: Analysing the process of desulphurisation of steel under slag with the average chemical composition of: CaO – 54.0%, Al_2O_3 - 30.2%, SiO_2 9.0%, MgO – 8.2%, and FeO content at the level of 0.94% drew attention to a high degree of desulphurisation at the level of 86%. Due to this fact it was possible to obtain high basicity of slag: V=CaO/SiO_2 at the level of 6.21. Mannesmann index, which characterizes the ability of slag to remove sulphur and non-metallic inclusions from steel and is defined as M=(CaO/SiO_2)/Al_2O_3, amounted to 0.21%-1 and was too low in comparison to the required one ranging from 0.35-0.45%-1. The calculations concerning the equilibrium chemical composition of slag, which determined the share of gas phase, liquid phase and solid precipitations, were performed using the thermodynamic software FactSage 6.2. These calculations showed that there were no solid precipitations present. The refining process under slag used in this research proved to be extremely efficient in terms of desulphurisation.

Research limitations/implications: It was concluded that the slag forming technology in the ladle is correct in terms of materials used, both as far as their type and amount are concerned. Deoxidation is efficient.

Practical implications: It is important to ensure that the furnace slag does not enter the ladle. As a result, it will be possible to improve the quality of the refining slag. Using the thermodynamic software FactSage 6.2 can contribute to modifying the chemical composition of the refining slag and result in an improvement of refinement as well as a better protection of the refractory lining of the ladle.

Originality/value: In order to calculate the equilibrium chemical composition of slag researchers used the thermodynamic software FactSage 6.2. Its use in practice can help select slag forming materials that are characterized by high refining parameters.

Keywords: Ladle furnace; Refining slag; Steel desulphurisation

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1. Introduction

Currently the production of liquid steel takes place in two stages. The first stage involves obtaining a semi-product in an arc furnace or in a converter, whereas the second stage consists in refining steel. Both processes take place in the presence of slag.

Irrespective of the device used refining steel in the ladle proceeds under a layer of specially formed ladle slag. The physical and chemical properties of slag decide about the quality of obtained steel and the technology used influences the economics of the process.

Slag used for liquid steel refining processes should be characterised by the following properties:

- it easily emulsifies in liquid steel – it happens when slag has low cohesion work, low viscosity and low melting temperature,
- emulsified slag particles easily flow out of steel – it depends on density and adhesion work,
- It has good refining properties in relation to sulphur and non-metallic inclusions present in steel, this slag should moisturize steel and non-metallic oxide inclusions and its adhesion work should be higher for inclusions than for steel.

Slag with determined properties is obtained thanks to using an appropriate amount of slag forming materials during the refinement process. It also requires the use of good quality materials. These materials in combination with the products from iron and admixtures oxidation together with impurities form slag.

Slag forming is a complicated process which depends on many factors such as the quality of materials used and the selected process. Slag forming materials (lime), reaction products and impurities dissolve in the obtained slag.

Ladle slag used in secondary metallurgy plays a very important role:

- steel desulphurisation,
- steel deoxidation,
- purification of steel from non-metallic oxide inclusions,
- ensuring proper chemical composition of oxide inclusions in ready-made steel,
- protection from the atmospheric influences,
- thermal insulation.

The process of removing impurities from steel is the most important of the all above mentioned roles.

2. Formation of refining slag

In order for refining slag to fulfil all these tasks it is necessary to use slag with an appropriate chemical composition. Carefully selected chemical composition allows to obtain desirable properties of slag and at the same time it ensures that the process will be conducted according to our assumptions. Steel refining process usually involves the use of slag based on CaO and Al_2O_3. This slag has non-oxidizing character, which means that when in use it should not cause oxidation of steel components with high oxygen affinity. It should ensure proper desulphurisation and removal of non-metallic oxide inclusions as well as the production of low oxygen steel.

To obtain proper refining slag it is necessary to select the main components carefully. It is important that after the dissolution of the components slag should have the lowest melting temperature – this allows the refining process of steel to be conducted efficiently. It is a rule that the melting temperature of such slag is lower than the temperature of steel. Decreasing the melting temperature can be done by adding aluminium oxide to the composition of the forming slag.

Refining slag formed on the basis of CaO and Al_2O_3 (containing CaO in the optimal range) ensures a decrease in the content of oxygen, sulphur and non-metallic oxide inclusions after the steel refining process [1].

Silica is an important component of the refining slag. It enters the refining slag during tapping from the furnace into the ladle or it is the product of silicon oxidation in steel. Silica causes the refining properties of slag to worsen as it reduces the assimilation of oxide phases in slag. It is believed that the silica content in slag intended for refining steel processes should not exceed 10%. On the whole, CaO, and Al_2O_3 are SiO_2 basic components of refining slag.

Figure 1 presents a three-component phase system of the CaO – Al_2O_3 – SiO_2 type. This is the basis for the composition and phases analysis of the obtained refining slag.

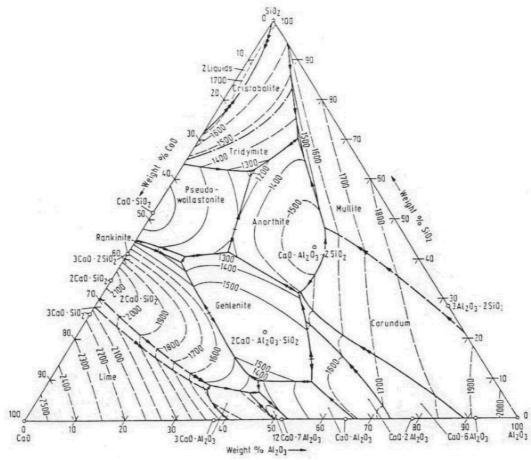

Fig. 1. Phase system CaO – Al_2O_3 – SiO_2[2]

Analysing Figure 1 one can notice a situation in which the amount of CaO or Al_2O_3 in slag is higher than 50%. What is more, it overlaps with the content of SiO_2 (right and left corner of the chart). There are also certain areas in the chart where slag has higher melting temperature than steel. In the middle part of the chart within the entire range of SiO_2 share one can notice complex compounds which have a significantly lower melting temperature than the metal that is being refined. As mentioned above, a significant share of SiO_2 in slag makes it impossible to obtain the required refining parameters. The main reason for this is the decrease in the basicity of slag despite obtaining low melting temperature of such slag.

Steelmaking practice shows that it is possible to select slag components depending on the types of steel produced. Figure 2 presents sample areas of the chemical composition of ladle refining slag in the system CaO – Al_2O_3 – SiO_2 selected for a particular steel refining purpose [2]. The areas marked 1-4 in Figure 2 characterize the following types of slag:

I – refining slag for "super pure steel" with low content of Al subject to calcium treatment, it has desulphurising and deoxidising properties,
II – wollastonite slag for steel intended for wires (cold treatment, e.g. tyre cords) and for high sulphur free machining steel,
III – slag used in the steel refining process to obtain products with high requirements when it comes to the quality of their surface (hydraulic cylinders, beating rolls, tracks of roller bearings); no desulphurisation, high absorption of Al_2O_3,
IV – ladle slag for steel used to produce roller bearings, deoxidation of C and Si without the addition of Al, no calcium treatment (high absorption of Al_2O_3) [2].

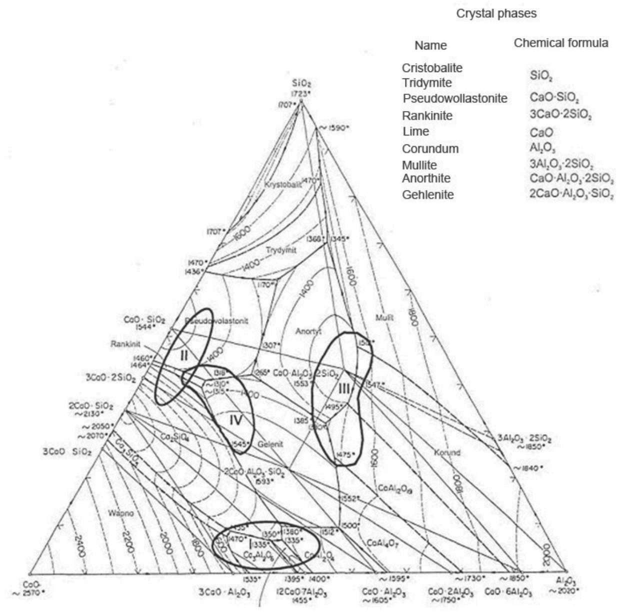

Fig. 2. Examples of chemical composition areas of steelmaking refining ladle slag [2]

Using the above mentioned information concerning the chemical composition parameters it is possible to determine the basic chemical composition of the refining slag. Carefully selected chemical composition can affect significantly the final content of impurities in steel by improving the efficiency of desulphurisation, removing non-metallic oxide inclusions and ensuring low content of oxygen in steel in the course of its refinement. Many steelworks have assumed that such slag should have a chemical composition similar to the one presented below: CaO: 45-55%, Al_2O_3: 25-30%, SiO_2 below 10%, MgO: 6-8%, FeO below1% [4-6]. Furthermore, in case of the refinement process whose aim is to obtain steel with low content of sulphur and non-metallic oxide inclusions it is recommended to use slag fulfilling the requirements of Mannesmann index, $M=(CaO/SiO_2)/Al_2O_3$.

Depending on the assumed technological conditions in a particular steelworks it may turn out that the employees working at the refining stations prefer lower content of aluminium oxide than that assumed in the composition of slag or that there are conditions in which slag can have low (several per cent) content of SiO_2. However, the final condition, i.e. the lowest FeO content in slag, is the main requirement when it comes to refining steel in the ladle efficiently and obtaining low content of oxygen in steel as well as minimal losses of components with high oxygen affinity. Last but not least, it is important to maintain low content of MgO, TiO_2 and Cr_2O_3 as they are detrimental to the flow and worsen the refining properties of slag. The presence of MgO in the presented range is, however, technologically founded due to its role in improving the durability of the refractory lining of the ladle. Obtaining slag with the above mentioned composition guarantees the production of very pure steel. Ladle slag is formed thanks to the addition of CaO, bauxite and specially made slag forming mixtures containing CaO and Al_2O_3. In order to form slag it is also possible to add slag made outside the furnace [3].

3. Own research

3.1. Research methodology

Obtaining high quality parameters of steel during the refining process in the ladle furnace depends mostly on using proper slag for the process. The purpose of this paper is to determine how the chemical composition of slag influences the effects of refining steel. Steel desulphurisation process was selected for this analysis. This process decides about the quality of the produced steel. The effectiveness of this process depends to a large extent on the character of slag used in the ladle furnace. The amount and type of added slag forming materials, however, plays a major role, too. It was assumed that refining slag parameters such as: basicity defined as $V=CaO/SiO_2$, Mannesmann index for slag $M=(CaO/SiO_2)/Al_2O_3$, and the amount of formed slag on the surface of liquid steel have a decisive influence on the steel desulphurisation process.

Research was conducted in a ladle furnace with the capacity of 65 Mg. The ladle furnace worked together with an electric arc furnace with the capacity of 70Mg. In order to obtain refining slag researchers used stable amounts of lime and slag forming mixture containing CaO 29-33%, Al_2O_3 24-32%, and small amounts of metallic aluminium 5-8%. 700 kg of lime and 100 kg of slag forming mixture were used. 10 melts for a selected chromium-nickel-molybdenum type of steel were conducted with a view to determining the influence of refining slag on the steel refining process. Samples were taken from these melts after the refining process was over in order to analyse their chemical composition. The analysis was performed using an XFR spectrometer TWIN-X (produced by Oxford Instruments).

Melting logs provided information on the course of the refining process, including desulphurisation of steel. In order to determine the influence of the amount and chemical composition of slag on the desulphurisation process, it was necessary to analyse the sulphur content in steel during the refining process.

Further stages of research involved equilibrium calculations concerning refining slag in given thermodynamic conditions. The calculations were performed with the aim of determining (with given temperature and pressure – in this case the atmospheric pressure and neutral atmosphere) equilibrium chemical composition of refining slag influencing the share of gas phase that is formed, liquid phase that has already formed and solid precipitations in progress of being formed in slag. The simulations were conducted using the thermodynamic software FactSage 6.2. Equilib is one of the most important modules of FactSage. This module was used in the course of the simulations of forming refining slag. The module is responsible for the Gibbs energy minimization. In the course of calculations it is necessary to provide chemical composition of slag and the conditions in which the process will be conducted (pressure, temperature). The research results were then analysed.

3.2. Research results and their analysis

Data from the conducted industrial research were presented in tables 1 and 2. The presented and described data will be used for an analysis of the steel desulphurisation process during its refinement in the ladle furnace.

Table 1.
Chemical composition of refining slag, its basicity and Mannesmann index for the analysed melts

Lp	CaO	Al_2O_3	SiO_2	MgO	FeO	V^*	M^{**}
1	46.3	36.2	9.8	12.0	0.60	4.72	0.13
2	63.6	20.8	9.3	5.9	0.86	6.84	0.33
3	49.6	30.1	10.5	8.2	1.21	4.72	0.16
4	48.7	31.5	11.0	10.4	1.51	4.43	0.14
5	56.8	29.8	8.6	7.2	0.80	6.60	0.22
6	52.2	29.1	10.5	10.4	0.58	4.97	0.17
7	56.8	31.0	7.4	6.3	0.56	7.68	0.25
8	51.2	30.8	9.0	9.2	1.36	5.69	0.18
9	56.9	32.5	7.2	5.1	1.05	7.90	0.24
10	57.8	30.1	6.8	7.4	0.90	8.50	0.28
Av.	*54.0*	*30.2*	*9.0*	*8.2*	*0.94*	*6.21*	*0.21*

$V^*=CaO/SiO_2$, $M^{**}=(CaO/SiO_2)/Al_2O_3$

Table 2.
Effectiveness of steel desulphurisation in the analysed melts

Lp	S_{final}, %	ΔS, %	η_s, %
1.	0.008	0.019	78
2.	0.005	0.034	87
3.	0.008	0.026	76
4.	0.005	0.029	80
5.	0.003	0.033	89
6.	0.004	0.039	91
7.	0.010	0.031	87
8.	0.003	0.029	84
9.	0.003	0.029	94
10.	0.004	0.036	90
Av.	*0.005*	*0.031*	*86*

An analysis of the chemical compositions of slag was conducted on the basis of research results obtained during the steel refining process in the ladle furnace. Table 1 shows that in the case of analyzed types of slag the content of particular components is consistent with the assumed contents of CaO, Al_2O_3 and SiO_2. The content of FeO is also at the level which ensures obtaining good effects of desulphurisation and low content of oxygen active in refined steel. Low content of FeO in slag proves that the refining process was conducted properly and that the deoxidation of slag during the refinement of metal proceeded efficiently. The presence of MgO in slag (within the range of 5.1-12.0%) was also recorded. Its presence in the analyzed slag can be explained by the fact that it is part of the slag forming mixture. MgO could also have been transferred from the refractory lining of the ladle.

High share of CaO in comparison to SiO_2 in the analysed slag guarantees that the basicity is high, which in turn improves steel desulphurisation. By analysing Mannesmann index from the chemical compositions of slag it is possible to conclude that it is too low in relation to the required values for slag used in steel refining processes targeted at obtaining low content of sulphur and non-metallic oxide inclusions. Increasing this index will be possible in research conditions if slag is prevented from entering the ladle during tapping. The analysis of chemical composition of different types of slag showed that in terms of their chemical composition (especially when it comes to the share of basic components) and low FeO content they can be an effective tool used in the steel refining process in the ladle. Referring back to Figure 2, one can conclude that the chemical composition of the obtained slag in terms of basic components is consistent with slag recommended for refining processes of high purity steel. It was possible to obtain good results when it comes to desulphurisation of steel under the layer of slag described above. As can be seen in Table 2 the desulphurisation degree of liquid steel in the ladle was high and ranged from 76-94%. The observed decrease in the sulphur content in steel amounted to 0.019 to 0.036%. The obtained final sulphur content in metal was at a very low level – 0.003 to 0.010%. This proves that the desulphurisation of steel was conducted efficiently despite different contents of sulphur in steel transferred for the refining process in the ladle furnace.

Figure 3 shows the relation between the calculated Mannesmann index for slag and the obtained degree of steel desulphurisation. In case of the analysed range of M index (0.13-0.28%$^{-1}$) it can be observed that its increase causes the desulphurisation degree to grow (within the range of 76-94%).

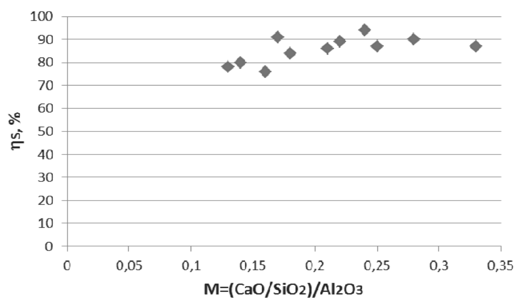

Fig. 3. The influence of Mannesmann index value on the desulphurisation degree of steel during the refining process in the ladle

Figure 4 presents the relation between the basicity of slag and the obtained desulphurisation degree of steel. The analysed range of slag basicity (4.43-8.5) showed that its increase causes the desulphurisation degree to grow within the range of 76-94%. In both analysed relations there were no major correlations from the statistical point of view. This is the result of many parameters (not only the composition of slag) which influence the efficiency of the desulphurisation process. Temperature is an important element that should be taken into consideration.

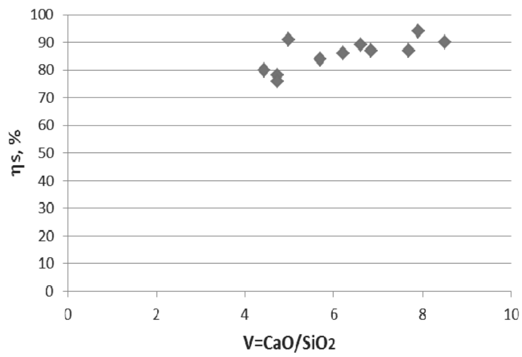

Fig. 4. The influence of the basicity of slag on the desulphurisation degree of steel during the refining process in the ladle

The next stage of the research involved equilibrium calculations concerning the refining slag in given thermodynamic conditions. The calculations were performed for given temperatures of the process, given stable pressure (in this case atmospheric pressure and neutral atmosphere). The purpose of performing these calculations was to determine equilibrium chemical composition of the refining slag and the share of gas phase in progress of forming, the liquid phase that has formed and solid precipitations. The simulations were conducted using the thermodynamic software FactSage 6.2. In the course of calculations for slag analysis their chemical compositions were provided as well as the conditions in which the refining process was conducted (temperature, pressure, type of atmosphere over the liquid slag). Calculations were made for the temperatures: 1400, 1500 and 1600°C, assumed atmospheric pressure and neutral atmosphere. The obtained results were presented in Table 3.

Table 3.
Solid phase share in the refining slag for given temperatures of the process.

Slag No.	1400°C	1500°C	1600°C
1	6.1	5.3	0
2	2.0	0	0
3	3.5	0	0
4	5.0	3.6	0
5	4.0	3.4	0
6	6.3	5.0	0
7	3.0	1.9	0
8	5.2	3.7	0
9	1.6	0.4	0
10	4.3	3.2	1.8

The calculations conducted for all slag types in given temperature conditions did not show the presence of gas phase in the chemical composition of slag. That is why Table 3 does not show its share. The presented values refer to solid phase that is formed in liquid slag. The liquid phase constitutes the remaining part (it complements the solid phase – up to 100%). The share of solid phase in slag presented in Table 2 refers mainly to solid precipitations, such as MgO. The temperature in the steel refining process ranged from 1509-1560°C at the beginning of the process and 1602-1685°C at the end. The calculated average temperature at the beginning of the process amounted to 1527°C and at the end 1634°C.

As can be seen in Table 3, in the temperature of 1500°C in case of the analysed slag the solid phase is present in the form of solid precipitations of the MgO type. In temperature of 1600°C in all but one case there is no solid phase. It is important to note that the biggest share of solid phase in temperature of 1500°C is present in slag which has MgO content higher than 9.0%. As far as ladle slag is concerned, MgO in contrast to CaO does not refine metal efficiently. However, its content in slag contributes to the protection of basic refractory lining of the ladle. As the calculations showed in temperature of 1600°C there are practically no solid inclusions in slag in the form of MgO. That is why it can be assumed that within the temperature range used for steel refining processes in the analysed MgO range (up to 12%) there is no solid phase in slag.

The conducted research showed that ladle slag with high basicity containing low content of SiO_2 and of Al_2O_3 allows to obtain liquid slag, which has low FeO content and is an efficient tool in the production of high purity steel.

4. Summary

Steel refining in the secondary metallurgy process allows to obtain high purity metal as long as proper slag is used in the steelmaking ladle. Refining slag must be characterized by certain properties which will guarantee its chemical competition. In order to refine steel efficiently it is also necessary to use an appropriate amount of slag in the ladle.

This paper analyses the refining process of chromium-nickel-molybdenum steel in the ladle furnace. This steel is intended for heat treatment, mainly to produce solid and built-up crankshafts. On the basis of the data from 10 melts it was possible to calculate main parameters which affect the process. The analysed parameters included: the chemical composition of slag, its basicity, Mannesmann index, desulphurisation degree and final sulphur content in steel.

Refining slag in the ladle (with the capacity of 65 Mg) was formed from 700 kg of lime and 100 kg of slag forming mixture containing CaO 29-33%, Al_2O_3 24-32%, as well as small amounts of metallic aluminium 5-8% and MgO 3-4%. As for the basic components, the slag obtained in experimental melts contained on average CaO – 54.0%, Al_2O_3 – 30.2%, SiO_2 9.0%, MgO – 8.2%. Thanks to such a composition it was possible to obtain high basicity of slag: $V=CaO/SiO_2$ at the level of 6.21. Mannesmann index, which characterizes the ability of slag to purify steel from sulphur and non-metallic oxide inclusions and which is defined according to the following formula: $M=(CaO/SiO_2)/Al_2O_3$, amounted to $0.21\%^{-1}$. According to the data the index for refining slag should range between 0.35 and $0.45\%^{-1}$. The obtained result of M index for slag in these melts shows values twice as high as those recommended in literature [7].

Slag used in the course of this research for steel refining process does not entirely play its role, i.e. it is to a smaller extent capable of assimilating non-metallic oxide inclusions. However, obtaining proper value of this parameter in practice is very difficult. This can be mostly attributed to the presence of SiO_2 in slag. Too big share of silica in slag is caused by furnace slag entering the ladle. The attempts to improve the refining properties of slag should include efficient control of furnace slag during tapping into the ladle. The obtained average FeO content in slag at the level of 0.94% contributes to low content of oxygen in refined steel. It shows how well deoxidation of slag proceeds during the steel refining process. It also has a positive influence on the desulphurisation process. The effect of desulphurisation in the conducted melts showed how efficient the desulphurisation was. Average sulphur content before the refining process was 0.036% S and in the ready-made steel it amounted to 0.005% S on average. The desulphurisation degree was high and amounted to 86%.

The presence of MgO in slag at the average level of 8.2% proves that this oxide is transferred to slag from the refractory lining of the ladle. The calculations of the equilibrium chemical composition of the refining slag influencing the share of gas phase, liquid phase and solid precipitations in slag were performed using the thermodynamic software FactSage 6.2. As a result of calculations the presence of solid precipitations in the form of MgO was recorded. These precipitations were recorded in the temperature of 1500°C.

It needs to be noted that the biggest share of solid phase in the temperature of 1500°C is present in slag in which MgO content is higher than 9%. In the temperature of 1600^0C in all cases but one there is no solid phase. In the range of the temperatures used during the steel refining process there are no solid precipitations in slag for MgO content up to 12%. As for the ladle slag, MgO in contrast to CaO does not have the function of refining metal. The presence of MgO within the range of observed values is a compromise between worsening the refining properties of slag and protecting the refractory lining of the ladle.

The use of the ladle furnace in steelmaking plants contributes to the improvement of steel quality, facilitates the work organization and lowers the production costs. The conducted analysis of the refining process in the ladle furnace shows that 85% of sulphur is removed from steel, which is a very good result. The steel obtained as a result of using high basicity slag has high quality parameters which fulfil the requirements of the recipient.

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References

[1] T. Lis, Metallurgy steel with high purity, Silesian University of Technology Publishing House, Gliwice, 2009 (in Polish).

[2] T. Lis, Desulphurisation of steel by using slag with regulated chemical composition, Metallurgist - News Metallurgical 5 (1994) 146-149 (in Polish).

[3] M. Dziarmagowski, J. Falkus, M. Karbowniczek, Z. Wcisło, J. Starczewski, Production method of the refining slag used in the manufacture of steel, Patent no. 181057 (in Polish).

[4] Z. Wcisło, M. Kruciński, M. Dziarmagowski, Steel Refining technology In VAD Process, Proceedings of the XIII Konferencje elektroocelaru a mimopecni zpracovani oceli, Rożnov pod Radhostem, Czechy, 1997, 156-160.

[5] T. Satek, Z. Buzek, The mutual comparison of operating results for LF and ASEA-SKF, Proceedings of the XIII Konferencje elektroocelaru a mimopecni zpracovani oceli, Rożnov pod Radhostem, Czechy, 1997, 161-166 (in Slovak).

[6] H. Krztoń, J. Pogorzałek, P. Różański, B. Smolec, Determination of reusability of slag, from afterfurnace treatment of liquid steel. Characteristics of ladle waste slag, Metallurgist - News Metallurgical 6 (2009) 394-399 (in Polish).

[7] J. Barański, U. Galisz, Ladle Furnace-unit for refining steel, Proceedings of the VI International Conference on Metallurgy, Rudy Raciborskie, 1995 (in Polish).