INFLUENCE OF REFINING ON ACHIEVING LOW OXYGEN CONTENTS AT PRODUCTION OF SPECIAL STEELS FOR ENERGETIC INDUSTRY

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Abstract

This paper deals with results of plant experiments aiming at achievement of low oxygen concentrations and high micro-cleanness during steel treatment for energetic industry on units of secondary metallurgy. Plants heats were aimed at analysis of influence of slag-making agents, wear of the lining, modification of inclusions, choice of mode of their out-stirring by the help of EMS and Ar blowing. Study of rules of formation, origin and conditions of elimination of non-metallic inclusions during steel treatment in ladle furnace ASEA-SKF was the aim of the experiments. Proper evaluation was made to determine oxygen concentration together with evaluation of micro cleanness according to DIN 50 602:1985 K4 and ISO 4967 Method A, namely on samples taken from the heel and under-head part of the forgings. Results present the oxygen concentration, number, ratio and analysis of chemical composition of non-metallic inclusions. Evaluation given in this paper presents the basic information on the achieved micro-cleanness at chosen refining technology. Results in this paper enable to point to the necessity of knowledge of the whole process of refining, which is crucial for achieving low oxygen concentrations and thus high micro-cleanness of steel.

Keywords: Steel, slag, secondary metallurgy, non-metallic inclusions, micro cleanness

1. INTRODUCTION

Nowadays, steel quality requirements are constantly increasing in the steel industry to achieve maximum production efficiency at minimum cost. Precondition for meeting these requirements is mainly to ensure a high cleanness steel, which is due to the non-metallic inclusions content but also gases and accompanying and trace elements. In order to achieve the required properties of the steel produced, not only choosing quality batch material, type of melting process and steel deoxidization, but also high technology of secondary metallurgy.

In terms of steel cleanness, there are two basic assessment points of view. The first one is chemical cleanness, which assesses not only the content of harmful elements, but also achieving the prescribed composition of steel. The second aspect is metallographic cleanness, which assesses the cleanness of steel in terms of non-metallic inclusions content. It is important to recognise that "steel cleanness" assessed by means of the above given aspects depends mainly on the steel quality (grade) and the required utility (mechanical) properties defined by the customer depending on the final product use [1]. In order to present different requirements for chemical and metallographic cleanness, **Table 1** gives examples that characterize different requirements placed on the final products with a different steel quality (grade) [2].

Metallographic cleanness assesses steel cleanness in terms of content of non-metallic inclusions that arise in the individual stages of steel production. The influence of non-metallic inclusions on steel cleanness and quality can be described using a variety of parameters, including their overall mount, morphology, shape, size, arrangement, etc. It is necessary to recognise that high content of non-metallic inclusions is the cause of problems arising during steel processing, such as casting, forming, thermal processing, and that non-metallic inclusions affect the properties of final products. Non-metallic inclusions cannot be removed completely; however, their negative influence can be reduced by minimizing the extent of their occurrence and improving the conditions for their removal or modification [3-5].

Table 1 Example of different requirements for cleanness for different steel grades [2]

Steel product	Maximum imcleanness fraction (ppm)	Maximum inclusion size (μm)
IF steel	[C]≤30, [N]≤40, T.O. ≤40 [C]≤10, [N]≤50	×××
Automotive & deep-drawing Sheet	[C]≤30, [N]≤30	100
Drawn and Ironed cans	[C]≤30, [N]≤30, T.O. ≤20	20
Alloy steel for Pressure vessels	[P]≤70	×××
Alloy steel bars	[H]≤2, [N]≤10-20, T.O. ≤10	×××
HIC steel (Hydrogen Induced Cracking)	[P]≤50, [S]≤10	×××
Line pipe	[S]≤30, [N]≤35, T.O. ≤30	100
Sheet for continuous annealing	[N]≤20	×××
Plate for welding	[H]≤1,5	×××
Bearings	T.O ≤10	15
Tire cord	[H]≤2, [N]≤40, T.O. ≤15	10
Non-grain-orientated Magnetic Sheet	[N]≤30	×××
Heavy plate steel	[H]≤2, [N]30-40, T.O. ≤20	Single inclusions 13 Cluster 200
Wire	[N]≤60, T.O. ≤30	20

* *T.O. - total oxygen content*

Progressive technologies enabling to meet these requirements involve the processes of secondary metallurgy, which represent an indispensable part in the process of modern production of steel. Secondary metallurgy includes a variety of refining processes, such as controlled steel deoxidization and steel alloying, homogenization of liquid steel, desulphurization of steel, removal of unwanted gases (hydrogen or nitrogen), modification of inclusions, improvement of micro cleanness and temperature adjustment by steel overheating defined according to the needs of the facility for continuous casting of steel, etc. The effect of individual secondary metallurgy methods can be summarized as follows [5,6]:

- *Inert gas blowing:*
    - *simple blowing (removing of inclusions, thermal and chemical homogenization of steel),*
    - *blowing with active slag (reaction of slag and metal; steel desulphurization),*
- *Injection of powder:*
    - *powder blowing using inert gas (steel desulphurization, modification of inclusions+ deoxidization of steel, steel alloying, steel decarburising),*
    - *injection of alloys in the form of filled steel profile (precise and economical steel alloying, modification of inclusions),*
    - *introduction of aluminium wire (controlled deep steel deoxidization),*
- *Steel refining using synthetic slag (steel deoxidization, controlled desulphurization, absorption of non-metallic inclusions),*

- *Vacuum degassing of steel:*
    - *ladle degassing,*
    - *stream degassing,*
    - *degassing in chamber (recirculation RH, lifting DH),*
    - *(reducing the content of [H] and [N], vacuum carbon deoxidization, steel alloying),*
    - *oxidation vacuuming of steel - VOD (production of corrosion-resistant steel - deep decarburization of chromium-alloyed steel),*
- *Refining of steel using gaseous mixture O_2 - Ar, or O_2 - H_2O in AOD, CLU converter (production of corrosion-resistant steel - deep decarburization at atmospheric pressure)*
- *Heating steel in ladle:*
    - *using electric arc at atmospheric pressure - LF,*
    - *using electric arc with a possibility of steel vacuuming - ASEA-SKF, VAD,*
    - *chemical heating - Al or FeSi oxidation at atmospheric pressure - IR-UT, CAS-OB,*
    - *chemical heating - Al or FeSi vacuum oxidation - ISSM.*

Using the individual above mentioned methods of steel processing within the aforementioned secondary metallurgy, different metallurgical (refining) capabilities were achieved (see **Table 2)**. A characteristic feature of modern secondary metallurgy is its diversity, when individual steel plants use secondary metallurgy in a complex form and choose a combination of devices, equipment and facilities which ensure that the required quality of steel corresponding to the increasing utility properties along with the possibilities of production optimization within the primary metallurgy (primary aggregates) is achieved.

Table 2 Metallurgical capabilities of individual devices for secondary metallurgy [5, 6]

Kind of secondary metallurgy	Element's content change				Alloying	ΔT (°C)	Inclusion's modifying
	ΔS (%)	ΔH (ppm)	ΔN (ppm)	ΔO (%)			
Argon homogenizing	-50/-60	+3/+4	0/+20	-50	Limited	-10/-15	No
Powder injection	-50/-80	+2/+5	+20/+40	-50	Big burn	-40/-60	Yes
Filled profiles' injection	-50/-80	0/+2	+0/+20	+/-	Excellent	-10/-15	Yes
Ladle furnace - LF	-50	+	+	-50	Excellent	+/-	No
Vacuum degassing station - VD	-70/-90	-60	-50	-50	Limited	- 50	No
Vacuum degassing station - RH	×××	-80	-30	-50	Excellent	- 50	No

The paper presents the results of operational experiments focused on achieving low concentrations of oxygen and high micro cleanness during processing steel for the needs of energy industry using the secondary metallurgy facilities and devices. The objective of the experiments was to study the principles of formation, origin and conditions for removing non-metallic inclusions during steel processing in the ASEA-SKF ladle furnace. The results will enable to point out the necessity of knowing the whole refining process, which is necessary for achieving low oxygen concentrations and thus also high micro cleanness of steel.

2. CHARACTERISTICS OF OPERATIONAL EXPERIMENTS

Operational experiments were focused on achieving low oxygen concentrations and high micro cleanness during steel processing using the facilities and devices of secondary metallurgy within the following production scheme: electric arc furnace EAF → controlled deoxidization during steel tapping in furnace → ASEA-SKF ladle furnace → pouring steel into moulds. The operational experiments were carried out during production of two grades of steel for energy industry, more precisely rotor steel for turbines. Its chemical composition is shown in **Table 3**.

The experiments were carried out by tapping the steel into the ladle after its processing in the electric arc furnace EAF. In order to achieve high micro cleanness and low oxygen concentrations in steel, deep deoxidization was carried out. In addition, during tapping a refining slag was added into ladle, whose properties should enable the subsequent desulphurization and capture of the maximum amount of non-metallic inclusions. After the start of tapping, first lime (CaO), then fluxing agent of corundum (Al_2O_3) type and subsequently aluminium (for steel deoxidization) were added.

Table 3 Basic chemical composition of rotor steels for turbines

Range	Basic chemical composition of grade A steel (wt.%)												
	C	Mn	Si	P	S	Ni	Cr	Mo	V	Al	H	N	O
Min.	0.27	0.30	×××	×××	×××	0.50	1.10	1.00	0.25	×××	×××	×××	×××
Max.	0.31	0.80	0.10	0.007	0.005	0.75	1.40	1.20	0.35	0.010	0.8 ppm	50 ppm	15 ppm
Range	Basic chemical composition of grade B steel (wt.%)												
	C	Mn	Si	P	S	Ni	Cr	Mo	V	Al	H	N	O
Min.	×××	×××	×××	×××	×××	3.40	1.40	0.30	×××	×××	×××	×××	×××
Max.	0.28	0.40	0.07	0.007	0.005	3.80	1.80	0.45	0.15	0.010	0.8 ppm	50 ppm	15 ppm

After tapping, the ladle with the steel and the slag formed was transported to the ASEA-SKF ladle furnace where the main part of the steel refining process took place. The steel refining process was separated into several parts: alloying, vacuum homogenizing, deep vacuuming and removal of non-metallic inclusions. Depending on the chemical composition of the slag, during the steel processing on the ASEA-SKF ladle furnace, either lime (CaO) or fluxing agent of corundum (Al_2O_3) type was added in order to increase the refining ability. In addition, prior to deep vacuuming modification of non-metallic inclusions by pure calcium was performed. The purpose of optimizing the slag regime was to increase the efficiency of steel refining on the ASEA-SKF ladle furnace in order to achieve the minimum oxygen concentration and high micro cleanness of steel. The processing on the ladle furnace was followed by bottom-pouring of steel into mould while producing polygonal forgings of 45, 55, 70, 85 and 95 ton weight.

In total, 9 melting processes of grade A steel and 8 melting processes of grade B steel were evaluated. During the operational experiments, samples of melt steel were taken for evaluation in order to determine the oxygen concentration. For sampling, the T.O.S. (Total Oxygen Sampling) device was used. Subsequently, combustion analysis was carried out. Moreover, slag samples were taken from the ladle after the following technological operations: after tapping from EAF, after vacuum homogenizing and after vacuuming with removal of non-metallic inclusions. Slag samples were analysed with a focus on their chemical composition. Finally, steel samples from forgings were taken, namely from the heel and under-head parts. The samples were evaluated with a focus on achieved micro cleanness according to DIN 50 602:1985 K4 and ISO 4967 method A.

3. RESULTS AND DISCUSSION

Evaluating the effectiveness of the rotor steels for the purposes of energy industry during the steel processing using the secondary metallurgy devices was carried out in several phases. Firstly, the slag regime controlling on the ASEA-SKF ladle surface was evaluated with the aim to achieve the minimum oxygen concentration in the grade A and B steel. Subsequently, micro cleanness according to DIN 50 602:1985 K4 and ISO 4967 method A was evaluated, namely from the forging heel and under-head parts of grade A and B.

3.1. Results of slag regime control on ASEA-SKF ladle furnace

The results of slag regime control on the ASEA-SKF ladle furnace for grade A steel are given in **Figure 1** and mean values of chemical composition are shown in **Table 4**. The achieved results of chemical composition for steel grade B are given in **Figure 2,** while the mean values of chemical composition are showed in **Table 5**. **Figure 1** and **Figure 2** describe chemical composition of slag entered in diagram CaO - SiO_2 - Al_2O_3 for 10 wt.% MgO.

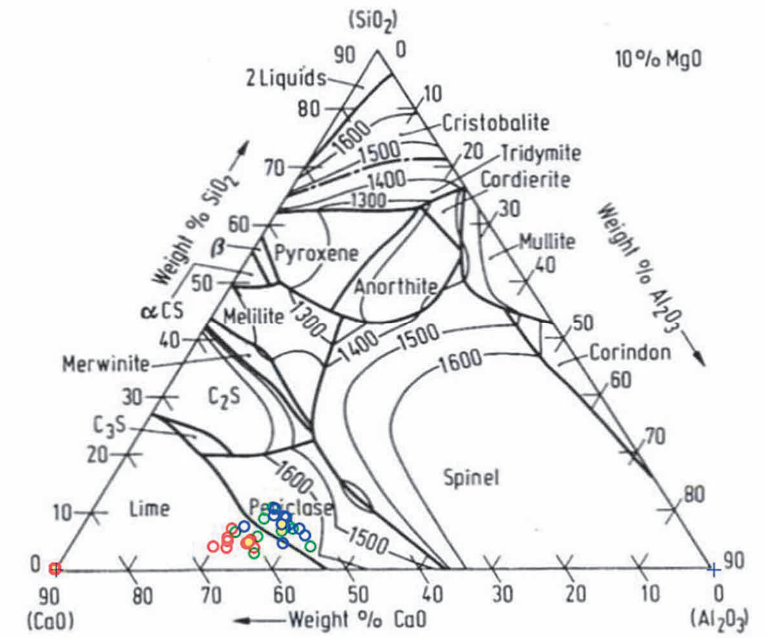


Figure 1 Slags type I, II and III in the diagram of CaO - SiO_2 - Al_2O_3 for 10 wt. % MgO for steel grade A

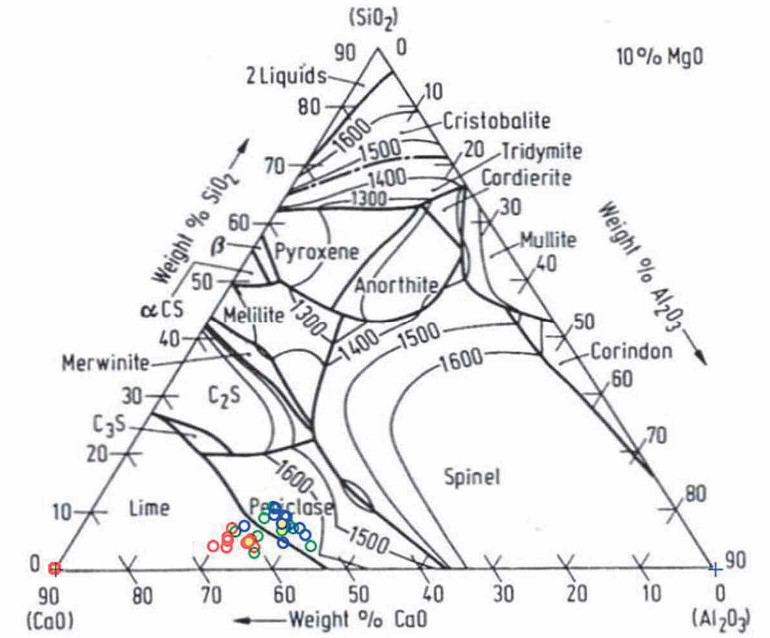


Figure 2 Slags of type I, II and III in the diagram of CaO - SiO_2 - Al_2O_3 for 10 wt. % MgO for grade B steel

Note: o *type I slag - slag after tapping from EAF;* ● *slag of type I - mean value*
o *type II slag - slag after vacuum homogenizing;* ● *slag of type II - mean value*
o *type III slag - slag after vacuuming and removal of non-metallic inclusions;* ● *type III slag - mean value*

Table 4 Mean values of chemical composition of grade A steel slags

Grade A steel	Mean values of slag's chemical composition (wt.%)						Basicity (1)
	CaO	MgO	Al_2O_3	SiO_2	Cr_2O_3	Fe_2O_3	
Slag I ●	57.46	8.03	22.64	4.33	0.72	7.66	2.53
Slag II ●	56.17	10.23	27.99	6.55	0.12	1.51	1.98
Slag III ●	55.19	10.29	27.32	7.61	0.12	1.61	1.89

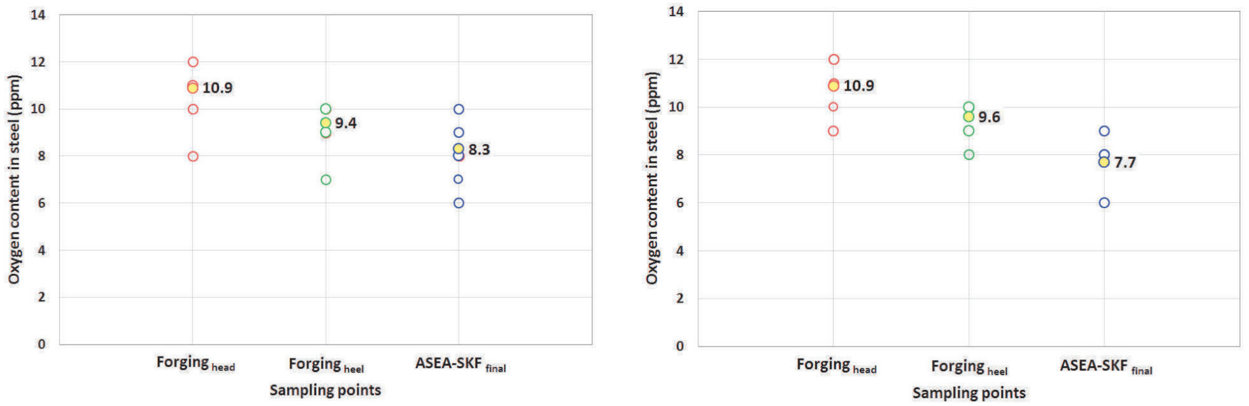
Table 5 Mean values of chemical composition of grade B steel slags

Grade B steel	Mean values of slag's chemical composition (wt.%)						Basicity (1)
	CaO	MgO	Al_2O_3	SiO_2	Cr_2O_3	Fe_2O_3	
Slag I ●	56.45	8.90	22.79	4.49	0.71	8.29	2.49
Slag II ●	56.66	12.53	26.34	5.99	0.14	1.58	2.15
Slag III ●	55.84	12.08	27.29	6.31	0.14	1.65	2.04

Slag regime controlling was influenced by the steel refining process, whose stages are alloying, vacuum homogenizing, deep vacuuming and removal of non-metallic inclusions. Slags of type I were taken during inserting the ladle into the carriage of the ASEA-SKF ladle furnace. These slags show high content of easily reducible oxides generated during the steel tapping into the ladle from the electric arc furnace (EAF) as shown in **Tables 4** and **5**. Slags of type I were (based on their chemical composition) subjected to adding lime (CaO) and fluxing agend of corundum (Al_2O_3) type in order to improve the refining abilities. Slags of type II were taken after vacuum homogenizing. The results show that the chemical composition has changed, as shown in **Tables 4** and **5**. This change was positively reflected in lowering the content of easily reducible oxides and increasing the content of Al_2O_3 in the slag. In addition, there was a change in the chemical composition of slag of type I from the area Lime into slag of type II to area Periclase for both A and B grade steel, as shown in **Figures 1** and **2**. Before the final treatment of steel, deep vacuuming, the inclusions were modified by pure calcium, both A and B grade steel. The last type of slag, type III, is slag taken after removal of non-metallic inclusions by electromagnetic stirrer (EMS) and argon (Ar). The resulting chemical composition of slags given in **Figures 1** and **2** show that the resulting slag of type III have lower dispersion in the achieved chemical composition than the types I and II.

The success rate of steel refining was verified by achieved oxygen concentration measured in the sample of bath after refining on the ASEA-SKF ladle furnace and in the forging. The results are given in **Figure 3a** (grade A steel) and **Figure 3b** (grade B steel)

The results presented in **Figure 3a** and **Figure 3b** show that the slag regime and individual technological stages of refining control within the secondary metallurgy enabled to achieve the oxygen concentration lower than 15 ppm (which is a value given by the Standard). The results of measuring oxygen concentrations also show a slight increase of oxygen concentration by max. 2 - 3 ppm. The reason of this slight increase in oxygen concentration in the heel and under-head parts of the forging compared to the concentration measured in the ladle is the passing of melt through argon curtain, mullite foundry ceramics and possible reactions during steel pouring or solidification in the mould.



a) steel grade A *b) steel grade B*

Figure 3 Oxygen content in A and B steel forgings and melts

3.2. Achieved micro cleanness of grade A and B steel forgings

The effectiveness of steel refining for the needs of the energy industry after casting, solidification and forging was evaluated on the rotor forgings. A micro cleanness test according to DIN 50 602:1985 K4 and ISO 4967 method A was performed on the material taken from the test area prescribed by the customer (heel and under-head parts).

Steel micro cleanness was evaluated in line with the standard DIN 50 602 K4, where all inclusions larger than 38 μm are recorded. In order to obtain more information on the inclusions size, next verification was performed according to the ISO 4967 method A, where all types of inclusions are recorded.

Metallographic samples preparation for micro cleanness testing according to the DIN 50 602:1985 K4 was carried out in the longitudinal direction, without etching [7]. Examining and documentation was performed at 100 time magnification. Micro cleanness evaluation was always performed on 12 samples with a total area of 1920 mm^2. The results of micro cleanness test according to the DIN 50 602:1985 K4 for the heel part of the forging are given in **Table 6.** The results for under-head part of the forging are given in **Table 7**.

Table 6 Mean results of the micro cleanness according to DIN 50 602: 1985 K4 for the heel area of forgings

Sample → ∅ results - heel	**K4/mm^2**	0	**Sulphides**	0	**Oxides**	0

Table 7 Mean results of the micro cleanness according to DIN 50 602: 1985 K4 for the head area of forgings

Sample → ∅ results - head	**K4/mm^2**	0	**Sulphides**	0	**Oxides**	0

From the results of micro cleanness testing presented in **Tables 6** and **7** is obvious that the forgings did not contain any inclusions larger than 38 μm. The achieved steel micro cleanness results were shown to the customer, therefore it was not possible to evaluate micro cleanness according to the K0 criterion.

For further micro cleanness evaluation, metallographic samples preparation was carried out in order to test micro cleanness according to the ISO 4967 method A [8]. It was performed in the longitudinal direction, without etching. Examination and documentation took place at 100 time magnification. Micro cleanness evaluation was carried out on the area of 322 mm^2 (300 fields). The results correspond to the worst field for each inclusion type and for each size series. The results of micro cleanness testing according to the ISO 4967 method A for the heel part of the forging are given in **Table 8.** Results for under-head part are shown in **Table 9**.

Table 8 Mean results of micro cleanness according to ISO 4967 method A for the heel area of forgings

Sample **∅ results - heel**	**Type A** **Sulphides**		**Type B** **Aluminates**		**Type C** **Silicates**		**Type D** **Globular oxides**		**Type DS** **Globular oxides**
	Thin	**Thick**	**Thin**	**Thick**	**Thin**	**Thick**	**Thin**	**Thick**	**×××**
Worst field	0	0	0	0	0	0	1	0.5	0.5

Table 9 Mean results of micro cleanness according to ISO 4967 method A for the head area of forgings

Sample **∅ results - head**	**Type A** **Sulphides**		**Type B** **Aluminates**		**Type C** **Silicates**		**Type D** **Globular oxides**		**Type DS** **Globular oxides**
	Thin	**Thick**	**Thin**	**Thick**	**Thin**	**Thin**	**Thick**	**Thin**	**Thick**
Worst field	0	0	0	0	0	0	1	0.5	0.5

The micro cleanness results given in **Table 8** and **Table 9** clearly show that the forgings did not contain any inclusions of type A, B, C, and inclusions of type D and DS were not larger than 13 μm.

4. CONCLUSION

In operating conditions, experiments were carried out in order to gain information on the formation, origin and conditions of removing non-metallic inclusions during steel processing within the secondary metallurgy. The following findings can be defined from the achieved results of the operating experiments:

- The results of the slag regime control on the ASEA-SKF ladle furnace showed that the addition of lime (CaO) and fluxing agent of corundum (Al_2O_3) type enabled to increase the refining ability of the ladle slag. This trend was reflected in the conversion of the slag type I chemical composition from the Lime area into slag type II to the Periclase area.
- From the resulting chemical composition of the slags type I, II and III it is clear that the final slags of type III have lower dispersion in the achieved chemical composition than the slags type I and II. This could be explained by the character of the individual slags: type I is primary ladle slag after tapping the steel into the ladle from the EAF. Type II is a ladle slag with an increased refining ability as a result of vacuum homogenizing. Type III is a final slag type after deep vacuuming and removal of non-metallic inclusions.
- The success of steel refining and the proposed slag regime was verified by means of achieved oxygen concentrations. The achieved oxygen concentrations during melt evacuation from the ASEA-SKF ladle furnace were below 10 ppm, which met the internal requirement of the steelworks. The subsequent forging casting slightly increases the oxygen concentration in the range of max. 2 - 3 ppm. However, the resulting oxygen concentrations in the final product are below the maximum value of 15 ppm as specified by the standard.
- The results of forging micro cleanness from the forgings weighing 45 - 95 tons show very good values not only according to the DIN 50 602:1985 method K4, but also according to the ISO 4967 method A, where the detailed analysis showed that the maximum inclusions size does not exceed 13 μm.
- The achieved micro cleanness of the forging determined according to the DIN 50 602:1985 K4 and ISO 4967 method A meet the customers´ requirements. It can be stated that the chosen refining technology and slag regime enable the production with a high repeatability while achieving the required micro cleanness.

ACKNOWLEDGEMENTS

The presented results were obtained as part of the solution of the technical development task of the PILSEN STEEL s.r.o. company named:

NEW DEOXIDATION, SLAG MODE AND LINING OF REFINING LADLE

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