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## SECONDARY STEEL REFINING FOR CONTINUOUS SEQUENCE BLOOM CASTING FOR HIGH OXIDE CLEANNESS FINAL PRODUCTS

### RAFINACJA POZAPIECOWA CIEKŁEJ STALI DO CIĄGŁEGO SEKWENCYJNEGO ODLEWANIA Z PRZEZNACZENIEM NA WYROBY O DUŻEJ CZYSTOŚCI TLENKOWEJ

Steelmaking and secondary refining process technology of resulphurized liquid steel with low content of total oxygen, assigned for continuous casting of strands for rolled and forged products for automotive industry was developed. The influence of secondary steel refining parameters on total oxygen content as well as amount and morphology of non-metallic inclusions was examined. It was found, that content of total oxygen and amount of non-metallic inclusions in steel decrease as steel refining time in the ladle becomes longer, and the chemical composition of non-metallic inclusions in steel changes from modified calcium aluminates to spinel inclusion of  $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{MgO}$  type. The total oxygen content in steel from continuous casting in four cast sequence ranged from 6 to 25 ppm, with percentage share of non-metallic inclusions from 0.09 to 0.30 per cent and equivalent diameter 0.78 to 1.59  $\mu\text{m}$ .

*Keywords:* secondary refining, oxide cleanliness, sequence continuous casting, steel product

Opracowano technologię wytapiania i rafinacji pozapiecowej ciekłej stali z regulowaną zawartością siarki, z niską zawartością tlenu całkowitego, przeznaczoną do odlewania w sekwencji wlewków ciągłych na wyroby walcowane i kute dla przemysłu motoryzacyjnego. Zbadano wpływ parametrów technologicznych rafinacji pozapiecowej stali na zawartość tlenu całkowitego oraz na ilość i morfologię wtrąceń niemetalicznych. Stwierdzono, że zawartość tlenu całkowitego w stali oraz liczność wtrąceń niemetalicznych zmniejszają się w miarę wydłużania czasu rafinacji stali w kadzi, a skład chemiczny wtrąceń niemetalicznych zmienia się ze zmodyfikowanych glinianów wapnia we wtrącenia spinelowe typu  $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{MgO}$ . Zawartości tlenu całkowitego w stali odlewanej w cztero wytopowej sekwencji wynosiły od 6 do 25 ppm, przy procentowym udziale wtrąceń niemetalicznych – od 0,09 do 0,30 % i średnicy równoważnej od 0,78 do 1,59  $\mu\text{m}$ .

## 1. Introduction

Material properties such as plasticity, fatigue strength, ultimate elongation and shock resistance of metals, and in particular structural steels used in automotive industry are mainly determined by non-metallic inclusions' properties, and primarily by size and number thereof.

Non-metallic inclusions in steel usually include sulfides, nitrides and oxides. Activity of the product of sulphur and nitrogen related inclusions release is much lower than of those with oxygen. Therefore, the problem with steel purity concerns mainly oxide inclusions [1]. Oxygen in solid state exists mainly in form of the said inclusions. Thus, the content of total oxygen in steel is representative for the amount of oxide inclusions. The

size of inclusions in liquid steel reduces along with reduction in the content of total oxygen.

In view of that the primary way to diminish oxide inclusions' particles is reduction in the total oxygen content in steel.

The present study takes up tests aimed at determining the impact of variable secondary refining time of low-alloy structural resulphurized steel, cast in the continuous caster for  $270\times 320\text{ mm}^2$  strand casting, in a 4-cast sequence, on the content of total oxygen, amount and character of non-metallic inclusions.

## 2. Foundations and metallurgical recommendations

The present expertise and experience in production of steel with high metallurgical purity is often called

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“clean steel”[1]. Results of thorough analysis in this regard [1, 2] have shown that in the case of a finished product of high metallurgical purity, steel melting process is of minor importance, while secondary refining and casting are crucial [1]. The main aim of secondary refining is fulfilment of the requirement concerning very low content of total oxygen in order to ensure low content of micro-inclusions. During steel casting, the most important thing is to avoid formation of inclusions from secondary oxidation of elements contained in steel.

Table 1 presents progress in reduction in the content of impurities in steel as well as development of secondary metallurgy processes along with vacuum treatment emergence, combination of vacuum with oxygen blast, ladle arc heating or chemical heating as a result of exothermic reaction of aluminum with oxygen or hybrid processes including vacuum treatment and heating in the same device [3].

TABLE 1  
Progress in aiming at reduction of the content of impurities in steel and development of secondary metallurgy processes [3]

Content	Year	1960	1985	2010	Future
Total oxygen		30	15	10 (6)	3-5
Carbon		250	50	15	10
Phosphorus		300	100	50	30
Sulphur		300	30	10	<10
Nitrogen		100	50	30	20
Hydrogen		6	3	1	<1
Processes development		1) vacuum treatment: RH/DH/TD→VOD/RH-OB→OMVR* 2) heating: ladle furnace/exothermal heating →OMVR* + heating 3) hybrid treatment: Asea-SKF/Finkl/VAD→OMVR*+ heating *vacuum reactor with optimum mixing			

Secondary treatment in ladle furnace constitutes a fundamental stage in removal of non-metallic inclusions from steel, by way of exchange between steel and slag. One of multiple functions of slag in ladle furnace treatment is to control the amount, shape, chemical composition, morphology and distribution of inclusions size [4-7] by proper chemical and physical properties, among which the following deserve particular consideration: density, viscosity and inter-phase tension. The higher slag density, the better impact of inclusions. Low content of surface-active elements (O, S) will foster separation of inclusions from slag. The best conditions for removal of inclusions from steel are achieved at low rates of inert gas flow with application of at least two profiles located in a proper manner on ladle bottom. [7, 8].

Layer of slag adherent to refractory lining of the ladle, called “ladle glaze” which is formed in worn-out or rarely used ladles, constitutes the main source of ex-

ogenous non-metallic inclusions in steel during its refinement [9-11].

Apart from oxides, which are the most popular, mixed oxide-sulfides also occur in steel. Aluminum oxide and calcium sulfide inclusions deteriorate castability of steel. Owing to introduction of calcium into liquid steel, oxide and sulfide inclusions may be modified. As steel temperature drops, sulphur solubility in steel is reducing and CaS is released, thus forming two-component inclusions – CaS or CaS-MnS and calcium aluminate [12]. Calcium treatment is used for regulation of MnS phases shape. For the purpose of effective modification of inclusions, calcium treatment should be effected at higher temperatures of liquid steel. Similar effect to Ca is produced by Rare Earths Elements (REE) in alloy form. Oxide-sulfides and REE sulfides, small, of spherical shape are characterized by expansion indices and elasticity modules similar to steel matrix; they effectively prevent from brittle cracking development along grain boundaries and have a positive impact on improvement of steel resistance to thermal fatigue [13].

Results of the recent research show increase in the content of total oxygen in steel, mainly as a result of its secondary oxidation during casting process [14-16]. In order to prevent it from occurring, improvement in the quality of refractory materials used in tundish is recommended, as well as casting with tight casing of the flux on the way ladle- tundish and tundish – mould, with cover and steel refining in tundish [20,21]. Simulation tests are more and more often used in manufacturing of high-purity steel (of controlled properties) for forecasting chemical composition of inclusions formed during cooling and solidification of liquid steel, in order to facilitate proper modification of the said inclusions during solidification.

In the industrial practice, in multi-cast sequence continuous casting, times of secondary refining of particular melts vary, and thus conditions of secondary treatment vary, affecting achievement of variable contents of total oxygen and non-metallic inclusions in concast strands.

### 3. Research

**Methodology.** Two series of tests were conducted, each of them composed of four-cast sequence of continuous casting of strands. In the first series heats were only subject to ladle furnace refining, 2 samples were taken from each heat by means of sampler for analysis of total oxygen (TOS-Total Oxygen Sampling). In the second series, two initial melts in the sequence were subject to vacuum treatment (VD) and the latter two were refined in ladle furnace. Samples for total oxygen marking were cut from rolled (final) material – bar of 50mm diameter.

Lateral metallographic specimens were prepared from TOS samples, first series, and were subject to microscopic examinations: by means of Nikon EPIPHOT 200 optical microscope for the purpose of numerical measurements of non-metallic inclusions, and by means of Inspect F electron microscope with EDS detector for the purpose of determination of the shape, size and chemical composition of inclusions.

Total oxygen in samples was determined by means of high temperature extraction.

**Execution of tests.** Industrial tests were conducted by continuous casting of four Cr-Ni-Mo low alloy steel heats with controlled content of sulphur, of chemical composition depicted in Table 2.

TABLE 2  
Chemical composition of steel for testing

Chemical composition, %							
C	Mn	Si	P	S	Cu	Cu+10Sn	Cr
0.18	0.70	0.15	max	0.017	max	max	0.40
0.23	0.90	0.35	0.035	0.035	0.35	0.50	0.60

Chemical composition, %							
Ni	Mo	Sn	O	N	Ca	Al	Ti
0.40	0.15	max	–	min	max	0.020	max
0.70	0.25	0.05	–	0.010	0.001	0.045	0.02

Steel was melt in arc furnace of the capacity 45 tonnes, subject to treatment in ladle furnace and subject to VD (vacuum degassing depending on requirements), and then cast in two-strand continuous caster for casting 270×320 mm<sup>2</sup> strands. Steel melt plant of HSW-Huta Stali Jakościowych Sp. z o.o. in Stalowa Wola is equipped with one arc furnace, three ladle furnaces and one VD/VOD facility. Preparation of steel for continuous sequence casting consists in preparation of melts in arc furnace, much earlier to casting and steel treatment in

ladle furnaces and VD facility. Thus durations of steel treatment in the ladle in one casting sequence vary significantly.

**Technology of liquid steel preparation for continuous sequence casting** is comprehensively described in study [22]. It covered respectively: comparison of charge and melting process in line with the binding instruction; steel melt with steel deoxidation by means of Al and supplementing alloying additives in form of ferroalloys, slag draining from ladle following melt, and introduction of the new one, composed of calcium and bauxite mix; refining of steel in ladle furnace, consisting in cautious mixing of steel with argon, improvement of alloying elements, change in chemical composition of refining slag by means of addition of slag forming material containing considerable volume of SiO<sub>2</sub>, in order to reduce alkalinity of slag, and prior to transfer to CCM – steel treatment by means of rod containing calcium-silicon and supplementing sulphur content by means of sulphur-containing rod. In case of vacuum degassing application in the ladle, it was effected following deoxidation, correction of alloying components and proper bath heating in ladle furnace, however prior to steel treatment with calcium and correction of sulphur content.

#### 4. Results

Table 3 presents results of determination of the content of total oxygen, amount, size and phase composition of inclusions in TOS samples taken at the beginning and at the end of steel refining in ladle furnace, melts of I series of tests. Table 4 presents results of similar determinations in samples taken from rolled bars, from melts subject to treatment in ladle furnace with and without vacuum degassing, II series of tests.

TABLE 3  
Content of total oxygen in steel, amount and size as well as phase composition of inclusions depending on duration of steel treatment in ladle (I series of tests, TOS samples determination)

No. of melt	Stage of LF process	Duration of ladle treatment of steel [min]	Content of O <sub>c</sub> in steel [ppm]	Surface share of non-met. Incl. [%]	Ø equivalent of non-metallic inclusions. [µm]	Phase composition of non-metallic inclusions
90893	beginning	190	–	–	–	–
	end		12 (15) <sup>1</sup>	0.09	0.78	MnS, CaO·Al <sub>2</sub> O <sub>3</sub> ·CaS
90895	beginning	145	26	0.23	1.01	MnS, MnO·SiO <sub>2</sub> ·CaO·Al <sub>2</sub> O <sub>3</sub> ·TiO <sub>2</sub>
	end		– (18) <sup>1</sup>	0.12	0.90	MnS, 2CaO·Al <sub>2</sub> O <sub>3</sub> ·MgO·CaS
90896	beginning	125	18	0.09	0.90	MnS, CaO·3Al <sub>2</sub> O <sub>3</sub> ·MgO
	end		23	0.21	0.99	Mn(Ti,Cr,Cu)S,CaO·Al <sub>2</sub> O <sub>3</sub> ·MgO·CaS
90897	beginning	110	–	0.22	0.97	MnS, MnO·SiO <sub>2</sub> , CaO·Al <sub>2</sub> O <sub>3</sub>
	end		25	0.13	0.92	MnS, CaO·Al <sub>2</sub> O <sub>3</sub> ·MgO

Notes: ( )<sup>1</sup> – content of total oxygen in rolled bar, diam.: 80 mm

TABLE 4

Content of total oxygen in steel, amount and size as well as phase composition of inclusions depending on duration of steel treatment in ladle (II series of tests, determination based on samples from rolled bars)

No. of melt	Secondary refining	Duration of ladle treatment of steel [min]	Content of $O_C$ in steel [ppm]	Surface share of non-met. Incl. [%]	$\emptyset$ equivalent of non-metallic inclusions. [ $\mu\text{m}$ ]	Phase composition of non-metallic inclusions
91891	LF, VD	130	8	0,13	1,59	MnS, CaO·2Al <sub>2</sub> O <sub>3</sub>
91892	LF, VD	100	9	0,30	1,37	MnS, CaO·2Al <sub>2</sub> O <sub>3</sub> ·MnS
91893	LF	190	12	0,20	1,27	MnS, CaO·Al <sub>2</sub> O <sub>3</sub> ·MgO·CaS
91894	LF	120	6	0,20	1,53	MnS, CaO·Al <sub>2</sub> O <sub>3</sub> ·MgO·MnS

Notes: LF – ladle furnace treatment; VD – vacuum degassing in ladle

Figure 1 presents characteristic non-metallic inclusions in TOS sample taken from liquid steel at the end of first sequence melt ladle treatment, cast following 190 minutes of ladle treatment, in I series of tests.

Figures 2 and 3 present characteristic non-metallic inclusions in sample taken from rolled bar, melt no.

91892, with ladle furnace refining and vacuum degassing of steel of 1st sequence melt of 2nd series of tests, with ladle treatment duration 100 minutes and melt no. 91893 respectively, with ladle furnace refining, 3<sup>rd</sup> sequence melt, II series of tests with the longest duration of ladle steel treatment.

Elements	1	2	3	4
<b>O</b>			34,7	5,6
<b>Mg</b>		1,0	5,4	0,6
<b>Al</b>		1,8	27,5	1,4
<b>Si</b>	0,2	0,2	0,7	0,1
<b>S</b>	15,2	23,8	0,5	14,8
<b>Ca</b>		8,8	13,5	13,3
<b>Cr</b>	1,0	1,1		1,0
<b>Mn</b>	11,0	13,8	0,3	2,8
<b>Fe</b>	72,6	49,6	17,6	60,6



Fig. 1. Characteristic non-metallic inclusions in TOS sample from melt no. 90893 (end of secondary treatment), ladle treatment duration 190 min, I series, magnification 1000x

Elements	1	2	3
<b>O</b>	27.6	21.5	
<b>Mg</b>	4.3	0.9	
<b>Al</b>	19.0	19.1	
<b>S</b>	20.4	28.4	55.7
<b>Ca</b>	4.2	9.3	
<b>Mn</b>	11.7	15.7	44.3
<b>Fe</b>	12.4	5.2	



Fig. 2. Characteristic non-metallic inclusions in the sample of rolled bar ( $\emptyset$  50 mm) from melt no. 91892 (LF, VD) ladle treatment duration 100 min, II series, magnification 1000x

Elements	% mass
O	31.5
Mg	7.8
Al	4.2
Si	0.6
S	0.4
Ca	21.3
Mn	0.3
Fe	33.9



Fig. 3. Characteristic non-metallic inclusions in the sample of rolled bar ( $\varnothing$  50 mm) from melt no. 91893 (LF) ladle treatment duration 190 min, II series of tests, magnification: 1000x

## 5. Analysis of results

Results depicted in Table 3 and Figure 4, presenting the relation between the total oxygen content in steel and steel ladle treatment duration indicate almost a linear drop in the said content as the time of steel treatment in the ladle is extended; longer ladle treatment of steel facilitates discharge of non-metallic inclusions.

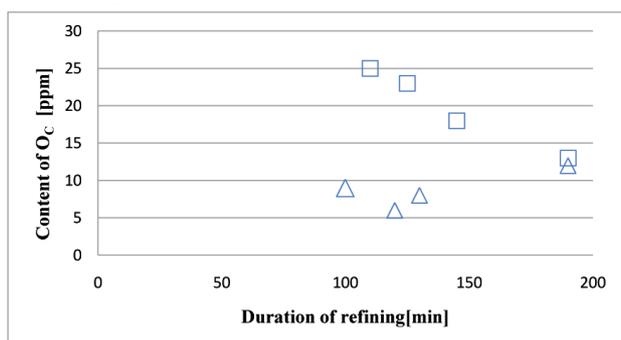


Fig. 4. Relation between total oxygen content in steel and type of secondary refining as well as duration of ladle treatment  
 □ – content of total oxygen in TOS steel, series I  
 Δ – content of total oxygen in finished product sample, series II

The content of total oxygen in steel in the 1st series of tests, in the range of clean steel was achieved only with the time of ladle treatment of steel equal to 190 minutes. Results of total content of oxygen in samples from rolled steel (series II), presented in Table 4, indicate a significant increase in total oxygen content as the time of ladle treatment of steel (LF treatment) exceeds considerably 120 minutes. In the case of steel melts with LF+VD treatment, when ladle treatment durations are comparable and close to 120 minutes, the contents of total oxygen are low and also comparable. Thus, extension of ladle treatment of steel above a certain limit results in the increment of the total oxygen content, resulting from transfer of inclusions from refractory lining to steel. This also indicates the presence of specific, modified

calcium aluminate inclusions, which include more MgO (7.8% Mg) than  $Al_2O_3$  (4.2% Al), as depicted in Fig. 3, and thus transform the inclusions into spinel, inclusions, hardly able to flow out. Moreover, this is also indicated by inclusions presented in Figure 1. Content of Mg in spinel inclusions is similarly high. In the case of shorter duration of steel treatment in the ladle, spinel inclusions with lower content of Mg (4.3%) are also recorded apart from aluminates.

Duration of steel treatment in the ladle has a clear and similar impact on the content of non-metallic inclusions measured with surface share of non-metallic inclusions. As it is depicted in Fig. 5, the surface share of non-metallic inclusions drops considerably as the duration of ladle treatment is extended, both in the 1<sup>st</sup> and 2<sup>nd</sup> series of tests.

Size of inclusions, measured with equivalent diameter on metallographic specimen of TOS samples, as it stems from data presented in table 3, oscillates around 1  $\mu$ m and is significantly lower than in samples from finished product (Table 4), ranging from 1.27 to 1.59  $\mu$ m. Smaller equivalent diameter of non-metallic inclusions in TOS samples as compared to samples from finished product stemmed from much higher cooling rate of the first samples. Data presented in tables 3 and 4 imply that the size of inclusions varies slightly in secondary refining, and it is reduced along with extension of ladle treatment duration. In samples of both series, MnS inclusions were found as well as  $MnO \cdot SiO_2 \cdot CaO \cdot Al_2O_3$ , inclusions at the beginning of refining (table 3) while  $xCaO \cdot yAl_2O_3 \cdot CaS$  as well as  $CaO \cdot Al_2O_3 \cdot MgO \cdot CaS (MnS)$  type inclusions were found at the end of refining (Table 3 and 4).

Increase in MgO content in inclusions, as the duration of ladle treatment of steel is extended (Fig. 1-3) indicates change in inclusions morphology – from modified aluminates with calcium sulphates into spinel inclu-

sions containing also calcium and manganese sulphates, however showing worse properties than aluminates.

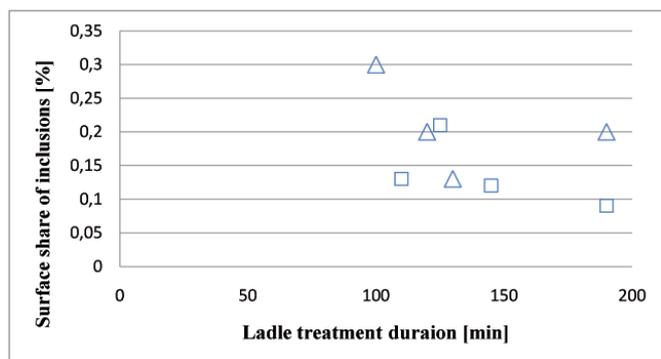


Fig. 5. Relation between surface share of inclusions in steel samples and ladle treatment of steel  
 □ – TOS samples, series I  
 △ – product samples, series II

## 6. Conclusions

Results of the conducted research lead to the following conclusions:

1. In the industrial conditions of the examined steel melt plant one may achieve the content of total oxygen in steel below 10 ppm, along with ensuring optimum castability, even in the conditions of controlled sulphur content,
2. The closer the duration of ladle treatment of steel to 140 minutes, the lower the content of total oxygen and non –metallic inclusions in steel,
3. Chemical and phase composition of non-metallic inclusions evolves, as the time of steel ladle treatment is extended, from modified calcium aluminates to spinel inclusions with MgO content, the volume of which increases along with ladle treatment extension.

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