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B. KALANDYK*, W. WOJTAL**

EFFECTS OF STEEL – APPLIED FOR LARGE-DIMENSION CASTINGS FOR THE POWER ENGINEERING – REFINING IN THE LADLE-FURNACE

EFEKTY RAFINACJI W PIECO-KADZI STALI STOSOWANEJ NA WIELKOGABARYTOWE ODLEWY DLA ENERGETYKI

The changes of a sulphur content during refining in melting low-alloy and high-alloy steels (G17CrMoV5-10; GX12CrMoNiVNbN9-1) applied for large-dimension castings for the power engineering are presented in the hereby paper. The investigated steel was melted in the oxygen-recovery melting technology with an application of maximum 70% of the process scrap. In addition, after steel melting in the electric arc furnace (EAF), the secondary metallurgy was performed in the ladle furnace (LF). It was shown that the application of the secondary metallurgy by a synthetic slag in the ladle furnace and argon bubbling of a metal bath leads to obtaining in the final analysis: 0.0043-0.0046% of sulphur (a decrease of S content during refining in LF reached 40%). Current measurements of FeO in the slag and maintaining its content below 0.8%, support obtaining such low sulphur content in steel. So low level of the slag oxidizing is one of the necessary conditions for a deep desulphurisation of the metal bath. Without the secondary metallurgy the sulphur content in low-alloy cast steel was 0.007%, while 0.01% in high-alloy cast steel.

Controlling of the gas (oxygen, nitrogen) content during steel melting and correcting the amount of additions (e.g. deoxidants), allowed to obtain the low oxygen content (below 45 ppm for two investigated steel grades) and nitrogen content (88 ppm for low-alloy steel and 330 ppm for high-alloy steel), which warrants a good combination of strength and plastic properties.

Keywords: Cast steel for power industry, Melting technology, Electric arc furnace, Ladle furnace, Desulphurisation

W pracy przedstawiono zmiany zawartości siarki podczas rafinacji w czasie wytapiania stali nisko- i wysokostopowej (G17CrMoV5-10; GX12CrMoNiVNbN9-1) stosowanej na wielkogabarytowe odlewy dla energetyki. Badaną stal wytopiono w technologii odzyskowo-tlenowej z zastosowaniem maksymalnie 70% złomu własnego. Dodatkowo, po wytopieniu stali w piecu łukowym (EAF) przeprowadzono obróbkę pozapiecową w pieco-kadzi (LF). Wykazano, że zastosowanie obróbki pozapiecowej żużlem syntetycznym w pieco-kadzi i argonowania kąpieli metalowej prowadzi do uzyskania w analizie końcowej 0,0043-0,0046%S (zmniejszenie zawartości S podczas rafinacji w LF sięgało 40%). Uzyskaniu tak niskiej zawartości siarki w stali sprzyja m.in. bieżący pomiar FeO w żużlu i utrzymanie jego zawartości poniżej 0,8%. Tak niski poziom stopnia utlenienia żużla jest jednym z warunków koniecznym do dobrego odsiarczenia kąpieli metalowej. Bez obróbki pozapiecowej zawartość siarki w staliwie niskostopowym wynosiła 0,007%, natomiast dla staliwa wysokostopowego 0,01%.

Kontrola zawartości gazów (tlenu i azotu) w czasie wytapiania stali i dokonywana korekta ilości wprowadzanych dodatków (np. odtleniaczy) doprowadziła do uzyskania niskiej zawartości tlenu (poniżej 45 ppm dla dwóch badanych gatunków stali) i azotu (88 ppm dla stali niskostopowej, 330 ppm dla stali wysokostopowej) gwarantująca dobrą kombinację właściwości wytrzymałościowych i plastycznych odlewów.

1. Introduction

The necessity of limiting contamination emissions by the conventional power engineering in accordance with the European Union Directives (Directive 2001/80/WE) is related to the modernisation and application of the modern steel and cast steel grades ensuring the improvement of the power units efficiency [1, 2]. That is why the power engineering increases its demands for high-quality castings (steam turbines elements, valve chambers etc.). Such tendency forces the foundry plants producing castings of large-dimensions, for the application of new cast steel grades (containing additions and micro-additions: W, V, Nb, N, Co and B) and implementation of modern innovatory technologies of melting steels containing the low content of harmful components (e.g. P, S) [3-6]. In a similar fashion, the low tendency for increasing the brittleness under casting operational conditions should be assured (increase of a brittle transition temperature).

In addition, growing production and electric energy costs as well as higher prices of alloying elements require searching for economic technologies, combining a high efficiency and low energy-consumption with as high as possible reclamation

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* AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, FACULTY OF FOUNDRY ENGINEERING, REYMONTA ST. 23, 30-059 KRAKÓW, POLAND
** ALSTOM POWER SP. Z O.O., STOCZNIOWCÓW ST. 2, 82-300 ELBLĄG, POLAND

TABLE 1

Chemical composition of the cast steel

Materials	C	Mn	P_{max}	S_{max}	Cr	Ni	Mo	N	Al	other
	% wt.									
G17CrMoV5-10	0.15 0.20	0.50 0.80	0.02	0.02	1.2 1.5	max 0.4	0.90 1.10	max 0.10	max 0.03	0.2-0.3%V max 0.3%Cu
GX12CrMoNiVNbN9-1	0.10 0.14	0.30 0.60	0.02	0.01	8.0 9.5	max 0.4	0.85 1.05	0.03 0.07	max 0.02	0.18-0.25%V 0.06-0.10%Nb max 0.3%Cu

of alloying elements from own foundry returns. Making an effort to meet these tendencies the Metallurgical Plant ALSTOM Power, which is specialising in large-dimension castings for the power engineering, prepared a long-range program warranting production of high-quality castings from ferrous alloys [7]. Implemented innovatory solutions allow for the increases of the plant capacity and economic effects [8].

The aim of the hereby paper is presenting the refining ability of the ladle furnace for the effective sulphur content decrease during melting low-alloy and high-alloy steels for large-dimension castings, when foundry returns are added to a charge (up to max. 70%).

2. Materials and methods

The effectiveness of the refining processes of steels, used for castings for power engineering, melted in the technology combining the arc furnace (EAF) with the secondary metallurgy in the ladle electric furnace (LF) was analysed on the grounds of randomly selected industrial melts of low- and high-alloy steels. The chemical composition of the investigated steel grades, acc. to EN 10213, DIN standards, are given in Table 1. Each time, a charge weight was approximately 25Mg. Melts were performed in the oxygen-recovery melting technology with using 45-70% of foundry returns. Gaseous oxygen was used for the oxidising process. Melting steel for large-dimension castings within this technology contains several operations. The following operations are performed in the arc furnace: melting, oxidising (C, P, Mn, Si), falling deoxidation and the preliminary refining by means of CaO and FeCaSi. After that, the tapping into the ladle is performed and then the ladle is directly transported to the ladle furnace stand, where the refining process with using the synthetic slag is carried out. In the final phase of the refining the correction of the chemical composition of the melted steel is performed. Then the modification process of cast steel is performed by powdered FeCaSi introduced in the steel by the cored wire.

During the melting process of the selected steel grades the measurements of the gases content in liquid metal and FeO content in the slag are performed by means of the device CELOX, using the proper testers. In dependence of the oxygen content in the metal bath the amount of the needed deoxidant was calculated, while in dependence of the FeO content the amount of the deoxidation mixture was calculated. The chemical composition analysis of non-metallic inclusions was carried out by the scanning microscope equipped with the EDS system of the IXRF Company for the X-ray microanalysis.

3. Discussion and results

An assurance of high mechanical and functional properties of steel applied for large-dimensions castings for power engineering is related to the necessity of performing the secondary metallurgy in the ladle furnace. It mainly results from the fact that harmful tramp elements such as phosphorus and sulphur strongly segregate in thick-walled cross-sections of castings, favouring formation of cold and hot cracks. Therefore a special attention is drawn to an effective decreasing these elements amounts during steel melting. Allowable contents of harmful elements in castings depend on their operational conditions, shapes and stresses. In castings of a complex shape, in which there is a danger of high stresses and in large-dimension castings, which are required to have high plastic properties, the sulphur content should be as low as possible. It is often recommended that the sum S and P will be lower than 0.025% [9]. The effective removal of S from the metal bath, during refining, requires a good deoxidation of this bath, a high slag basicity at a low oxidation degree of layers within the interfacial metal-slag area. The typical refining slag is of basicity app. 2 (CaO/SiO_2), at the FeO content in the slag being within the range: 0.3 - 1%. Under such conditions S can be removed to the content of 0.008 - 0.01% [3, 5]. Obtaining still lower S content in cast steel allows an application of the synthetic slag based on $CaO\text{-}SiO_2\text{-}Al_2O_3$ (in addition, Al_2O_3 decreases a slag viscosity, which – in turn – increases the desulphurisation process rate of the metal bath). The argon bubbling process favourably influences desulphurisation of the metal bath during refining in the ladle furnace. In this case, mixing of the metal bath significantly increases the S-exchange coefficient between the slag and metal bath [10, 11].

A gradual introduction of powdered FeCaSi in a core wire, which allows the prolonged maintaining of the Ca content within limits close to its solubility, influences favourably a better utilisation of Ca for desulphurisation. In this case, the desulphurisation rate will be the sum of the sulphur reaction with reagents originated from the slag and originated from the powdered refiner [6]. Thus, the desulphurisation rate can be presented by the following equation:

$$-\frac{d[\%S]}{dt} = \left(\frac{d[\%S]}{dt}\right)_{slag} + \left(\frac{d[\%S]}{dt}\right)_{powdered\,refiner}$$

In this case, such desulphurisation of the metal bath by means of FeCaSi favours the modification of shapes of large Al_2O_3 dendrites into finer, spheroid aluminates, rich in CaS.

On the grounds of the obtained results, it was found that steel melting in the technology: arc electric furnace and ladle furnace (EAF+LF) assures obtaining the low S content, at the level of 0.0043 % S and 0.0046% S in low-alloy and high-alloy cast steels – respectively (Fig. 1). The application of the combined technology of the steel melting (EAF+LF) assured lowering of the S content in steel melts by app. 60%. The results presented in Figures 1 and 2 indicate also that the desulphurisation process occurred during the refining in the ladle furnace (the S content during refining in LF decreased by app. 40%). Such low S contents, in the final analysis (LF-2), were obtained due to a good oxidation, application of the synthetic slag, argon bubbling through liquid metal, application of FeCaSi in a core wire guard and controlling the FeO content in the slag during refining. The FeO content in the refining slag during melting low-alloy steel was equal 0.6 - 0.8%, while during melting high-alloy steel it was within range 0.3 - 0.8%.

Phosphorus can be removed only at the beginning of steel melting in the arc furnace. The observed, negligibly increased, P content during the refining in the ladle furnace (LF) results mainly from this element presence in ferroalloys introduced to supplement the steel chemical composition (Fig. 3) [12].

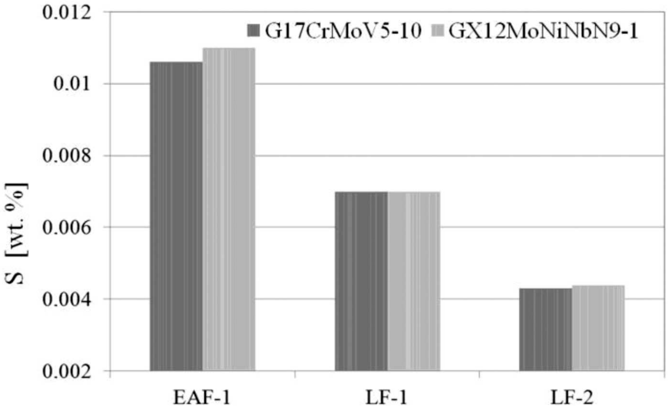


Fig. 1. Changes of the S content during melting steel for castings for the power engineering in the EAF+LF process; EAF-1, LF-1 – at the beginning of the melting process; EAF-2, LF-2 – at the end of the melting process in EAF and LF

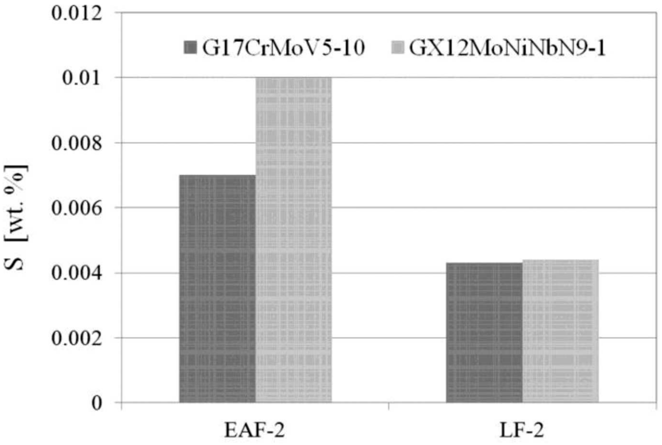


Fig. 2. The S content in the second sample (final) from EAF and from LF

Carrying out measurements of gases contents during the steel melting contributed to the optimisation of the deoxidation process by introducing deoxidants in amounts properly choosed to the oxygen amount dissolved in the bath. In effect, the low content of oxygen was obtained in the final analysis of the melted steel. For both steels (low- and high-alloy) the oxygen content did not exceed 45 ppm (Table 2), while nitrogen content was lower than the allowable values (for low-alloy steel the average nitrogen content was 85.3 ppm, and for high-alloy steel 325 ppm).

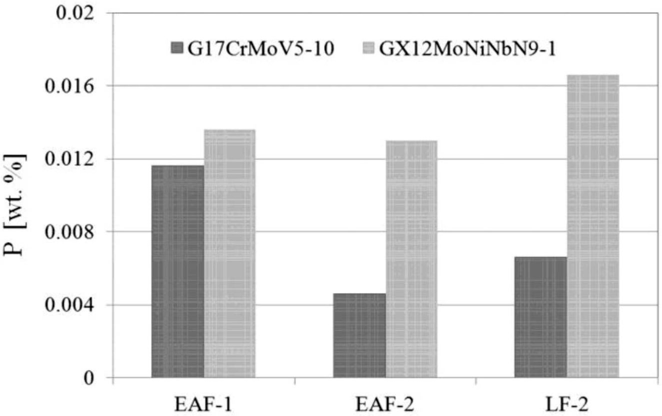


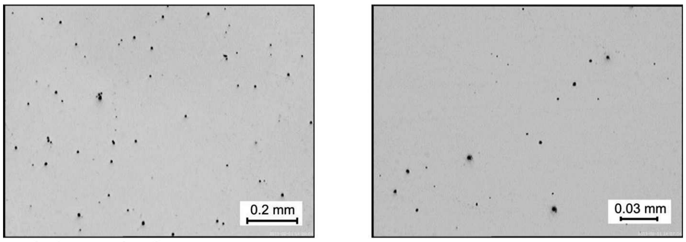
Fig. 3. Changes of the P content during the steel melting in the process EAF+LF

TABLE 2

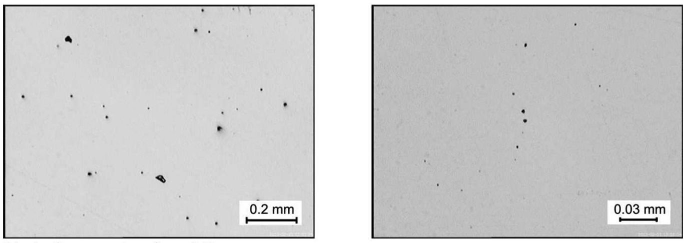
Oxygen and nitrogen content in the final analysis of the investigated cast steel grades

Materials	No. of melts	Oxygen [ppm]		Nitrogen [ppm]	
		content	average	content	average
G17CrMoV5-10	1 2 3	37 36 27	33.3	85 83 88	85.3
GX12CrMoNiVNbN9-1	1 2 3	45 43 38	42.0	330 327 320	325.0

Deep desulphurisation and degassing of liquid metal in the ladle furnace leads also to the effective decreasing of non-metallic inclusions (Fig. 4). At the end of the liquid metal treatment in the ladle furnace the presence of not numerous, large (up to ~5 μm) spherical oxides inclusions enriched in such elements as: Al, Ca, Mg and Fe were found (Fig. 5, Table 3). Another kind of observed precipitates were the ones of irregular shapes and sizes not exceeding 1.5 μm (Fig. 8). These precipitates are mainly manganese sulphides occasionally enriched in Ti and V (Fig. 9, 10, Table 4). The presence of Ti and V in these precipitates originated from the introduced, in the final stage, ferroalloys of titanium and vanadium. Decreasing of the S content to 20-60 ppm, which is obtained in the final stage in ladle furnace (LF) caused the elimination of mixed precipitates, where MnS constitutes the oxygen envelope. Such precipitates are numerous in steel containing approximately 150 ppm of S [11].



a) before tapping from EAF



b) before tapping from LF

Fig. 4. Non-metallic inclusions during the steel melting in the EAF + LF process

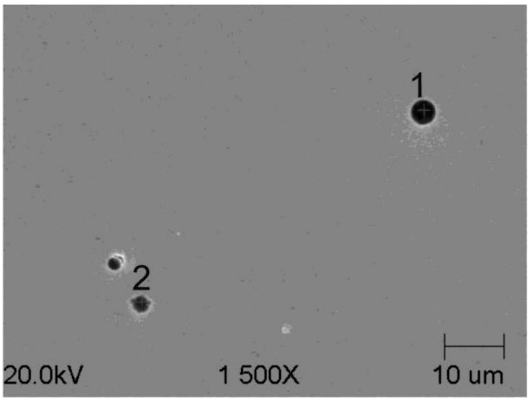


Fig. 5. Non-metallic inclusions in the metal bath in ladle furnace (LF)

TABLE 3

The chemical composition of inclusions from Fig. 5, determined by the X-ray microanalysis method

Area	O	Mg	Al	Si	Ca	Fe
	% wt.					
1	25.3	2.8	24.8	1.2	18.3	27.6
2	19.6	9.5	19.9	0.4	2.2	48.3

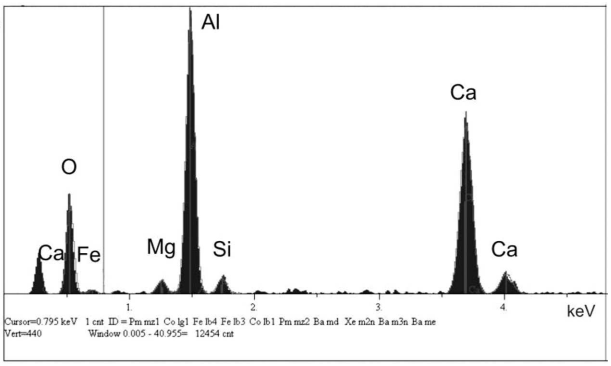


Fig. 6. X-ray spectrum with the energy dispersion (EDS) – from point 1 in Fig. 5

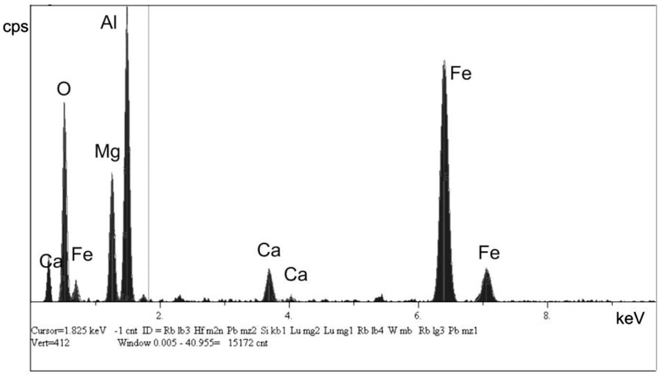


Fig. 7. X-ray spectrum with the energy dispersion (EDS) – from point 2 in Fig. 5

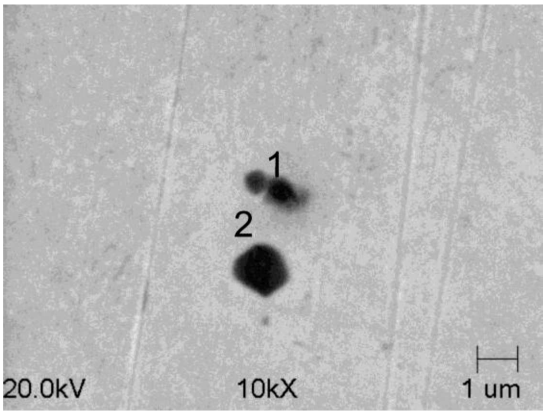


Fig. 8. Non-metallic inclusions in the metal bath in ladle furnace (LF)

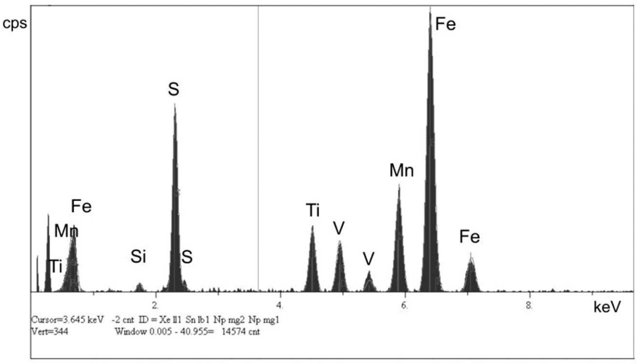


Fig. 9. X-ray spectrum with the energy dispersion (EDS) – from point 1 in Fig. 8

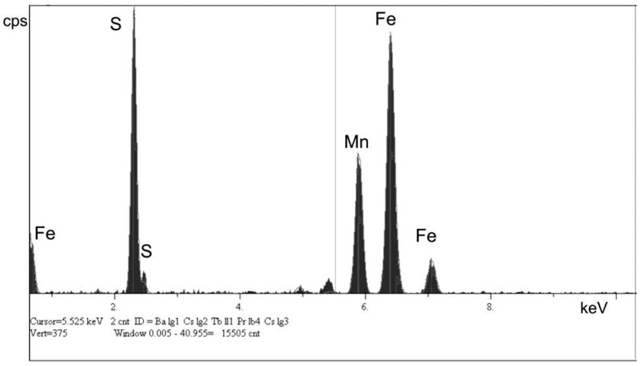


Fig. 10. X-ray spectrum with the energy dispersion (EDS) – from point 2 in Fig. 8

TABLE 4

The chemical composition of inclusions from Fig. 8, determined by the X-ray microanalysis method

Area	Mn	S	Ti	V	O	Si	Fe
	% wt.						
1	15.4	12.4	6.4	5.1	1.3	0.8	58.6
2	22.7	18.6	-	-	2.4	-	56.3

Decreasing harmful additions (P, S) and gases, as the result of the application the steel melting technology EAF+F, leads to obtaining good strength and plastic properties of large-dimensions castings (Table 5).

TABLE 5

Example of mechanical properties of cast steel applied for large-dimension castings

Materials	UTS [MPa]	YS [MPa]	EL [%]	Impact energy [J]	Ra [%]
G17CrMoV5-10 required	590 780	min 440	min 15	min 27	
received	701 689	566 576	21 22	105 108	66 64

4. Conclusions

- Decreasing of sulphur content during subjecting low-alloy steel to the oxygen-recovery melting technology, with the application of maximum 70% foundry returns, occurs faster and easier than during melting high-alloy steel.
- The effectiveness of the liquid metal refining in the ladle furnace ensures obtaining the very low sulphur content in the after-tapping analysis (0.0043 - 0.0046%). Such deep desulphurisation effects can be obtained when: the synthetic slag, FeCaSi in the cored wire, argon bubbling of the metal bath and maintaining FeO content in the slag below 0.8% - is applied.
- The phosphorus content can be lowered only during the oxidation process in the arc electric furnace. For the low-alloy cast steel the phosphorus content was 0.004 - 0.009. However, in case of high-alloy steel the phosphorus content was higher and equalled 0.016 - 0.017%. An increased P content in liquid metal during refining in the ladle furnace results from the P presence in introduced ferroalloys.
- The oxygen content in the investigated low-alloy steel was 27 - 39 ppm while in the high-alloy one 38 - 45 ppm. Such low values of the oxygen content can be obtained due to controlling carried out during the melt performing and correcting the deoxidant amount.
- The secondary metallurgy in ladle furnace influences also decreasing non-metallic inclusions leaving not numerous spherical oxide inclusions of the size up to 5 μm enriched in Al, Ca, Mg and fine irregular inclusions of manganese sulphide (<1.5 μm) enriched in Ti and V, originated from the introduced ferroalloys.

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