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INTENSIFICATION OF LOW-CARBON STEEL DESULPHURISATION IN THE INDUCTION FURNACE

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ABSTRACT

Sulphur in steel is an undesirable element because it lowers all technological and uses values of steel products. During the steelmaking process, the desulphurization process depends on the thermodynamic conditions, the used desulphurizes, and the stability of the formed sulphides. The desulphurization technology in the production of low-carbon steel in a protective atmosphere, with the addition of synthetic slag and strong desulphurizing agents with additional argon blowing, is presented in this paper. The reduction of sulphur content achieved in the induction furnace is an important contribution to the technology of the production of low-carbon steels.

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1. INTRODUCTION

Sulphur in steel occurs in all processes of production of liquid steel in lower or higher contents and is a harmful impurity because it reduces the mechanical properties, weldability, anticorrosive, electrical and other properties [1].

The harmful effect of sulphur is already expressed at the content of 0.005 – 0.010%, and in some cases at significantly lower values. Sulphur has unlimited solubility in liquid steel and very limited solubility in solid steel. Due to the reduction of solubility, during the solidification and cooling of steel, sulphur is excreted from the melt in the form of sulphide eutectic and collects at the grain boundaries. This eutectic has a very low melting point (988 °C) and is further reduced if oxygen is present in the eutectic, which leads to the appearance of eutectic type FeO-FeS (940 °C), which weakens the bond between grain and causes "red fracture". To reduce the harmful effect of sulphur on steel properties, efforts are made to produce steel with the lowest possible sulphur content and with sulphide inclusions that have a predominantly globular shape and do not deform during hot plastic processing.

Sulphide and oxysulphide inclusions are deformed during hot processing and especially MnS inclusions spread in the longitudinal direction in the direction of rolling, which causes anisotropy of the steel properties.

The addition of calcium can affect the transformation of sulphide inclusions, with undesirable MnS inclusions being converted to CaS inclusions, while solid aluminates are transformed into liquid calcium aluminates. By injecting CaSi or Ca, modification and calcium sulphide are achieved. A minimum Ca/S ratio is required to achieve complete modification. In steels, these aluminates are

covered with a thin layer of complex Mn and Ca sulphides, Figure 1.

With the increasing content of CaS in mixed crystals (Ca, Mn) S, there is an increase in sulphide hardness. In plastic processing, sulphides in which MnS predominates are deformed, while sulphides in which CaS predominates retain their original form, Figure 2. As the CaS content increases, toughness increases in all directions and increases the isotropic properties of steel.



Figure 1. Schematic representation of the modification of the inclusions [1]



Figure 2. Morphology of sulphide inclusions in steel CaS (left) and MnS (right) [2]

In the integral production of clean steel, the control of sulphur content is of particular importance [3]. Desulphurization of steel implies optimization of the chemical composition of the slag using different agents, taking into account the increase in productivity and the reduction of production costs [4]. Most of the desulphurisation takes place through the reaction between magnesium and sulphur in the bath. The formed MgS ascends to the slag layer and reacts with lime to form CaS [5].

1.1 Technological procedures for sulphuring

The desulphurisation process depends on the thermodynamic conditions, the used desulphurizes and the stability of the formed sulphides. Achieving low sulphur contents in steel is not only a metallurgical but also an economic problem. Thermodynamic and kinetic conditions for good desulphurization are sometimes opposite to the realization of some other metallurgical processes, such as oxidation, phosphorus removal and others [6]. Conditions for good desulphurization are:

• high CaO activity;

- low oxygen activity;
- the ability of slag to dissolve CaS.

In addition to thermodynamic factors, kinetic factors are important for the desulphurization process, among which the most important are [7]:

- good slag fluidity;
- size of the contact surface between metal and slag;
- mixing intensity of metal and slag phase;
- influence of the gas phase.

2. EXPERIMENTAL PROCEDURE

The experimental part of this work was done at the Institute "Kemal Kapetanović" in Zenica, in the Department of Melting and Casting. The tests aimed to determine the effect of desulphurization agents as well as additional mixing of liquid melt with inert gas on the desulphurization efficiency [8].

The technology of making test melts in an induction furnace consisted of the following phases:

- 1. charge preparation;
- 2. charge melting;
- sampling for chemical analysis of metals and slag, with temperature measurement;
- 4. removal of primary slag;
- 5. addition of synthetic slag;
- 6. blowing the melt with argon (5 min);
- 7. sampling for chemical analysis of metals and slag, with temperature measurement;
- 8. addition of strong deoxidants to the melt;
- 9. blowing the melt with argon (10 min);
- 10. sampling for chemical analysis of metals and slag, after 1 min of blowing, 5 minutes and 10 minutes;
- 11. monitoring the temperature during blowing and maintaining the temperature within the set limits;
- 12. pours melt into moulds.

An induction furnace with a capacity of 50 kg was used to prepare the starting material. The T-1 melt was made of low-carbon steel of the chemical composition given in Table 1.

Table 1 . Chemical composition of starting material [8]	
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Molt	Chemical composition, %									
Men	С	Mn	Si	Р	S	Cr	Ni	Мо		
T-1	0.22	0.54	0.10	0.024	0.025	0.20	0.10	0.03		

After cooling ingots (4.5 - 5 kg) were prepared from the starting melt for the re-melting in the vacuum induction furnace. The vacuum induction furnace with a capacity of 20 kg with a sintered magnesite refractory lining was used.

Argon purge was performed from above and desulphurization was achieved using synthetic slag and complex alloys of CaSiAl and CaSiMg.

Chemical composition (Table 2) is the most important characteristic of slag because it determines its basic physical and chemical properties. The composition of slag is determined based on the fact that the basic component is CaO as well as that the basicity of slag must be as high as possible, taking into account its viscosity at processing temperatures.

The best effect is in terms of reducing the sulphur content as well as oxygen observed in the treatment of steel with calcium [1]. Therefore, Ca-based desulphurizes (CaSiAl and CaSiMg) were selected, which were added in an amount of 1-3 kg / t. and their chemical composition is given in Table 3..

Table 2. Chemical composition of added synthetic waste [0]	Table 2. Chemical	composition	of added s	synthetic waste	[8]
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	Composition slag I			Composition slag	П
CaO	0.233 kg	64%	CaO	0.112 kg	32%
SiO ₂	0.053 kg	14%	Al ₂ O ₃	0.063 kg	18%
CaF ₂	0.080 kg	22%	CaF ₂	0.175 kg	50%
total	0.366 kg			0.350 kg	

Table 3. Chemical composition of
desulphurizes

CaSiAl		60% Ca	30% Si	10	% Al
CaSiMo	J	60% Ca	30% Si	5%	Mg
Melting	was	performed	under	an	argon

atmosphere. Argon flow is turned on during the melting period to prevent oxidation of the steel melt.

After the raw materials for smelting are charged, melting is performed at maximum power. When all charges is melted, a sample was taken for chemical analysis. The formed amount of slag was removed, and after reaching the prescribed temperature, (1590 °C - 1610 °C), alloying was performed.

Melting and refining in the furnace were performed under the protection of argon. Argon was blown with 0.006 L/min through the asbestos-cement cover of the furnace. FeMn, FeSi and graphite were added through the same cover. The cover was removed when synthetic slag was added and when CaSiMg and CaSiAl were added using an immersion bell.

The chemical composition and temperatures of steel in an induction furnace and the final chemical composition of steel are shown in Table 4 as well as the chemical composition of slag in Table 5. The desulphurization process requires high basicity slag and reducing conditions.

Table 4. Chemical composition of steel and overview of measured temperatures [8]

MELT	Teet	Temp.	Cł	nemical co	Cumthatia alag			
IVIEL I	Test	°C	С	Mn	Si	S	Р	Synthetic stag
	1	1610	0.20	0.91	0.30	0.037	0.017	
V1	2	1615	0.19	0.91	0.14	0.019	0.017	
	3	1615	0.21	0.88	0.24	0.015	0.017	SLAG I
	4	1610	0.22	0.85	0.21	0.014	0.017	Cashvig
	5	1610	0.23	1.00	0.32	0.013	0.017	
	1	1600	0.18	0.65	0.21	0.027	0.019	
	2	1600	0.27	0.69	0.20	0.027	0.019	
V2	3	1600	0.24	0.70	0.35	0.018	0.019	SLAG I CoSiMa
	4	1600	0.27	0.70	0.33	0.014	0.019	Castiviy
	5	1600	0.29	0.72	0.37	0.012	0.020	
	1	1600	0.25	0.55	0.15	0.038	0.020	
	2	1560	0.24	0.52	0.08	0.036	0.023	
V3	3	1600	0.22	0.56	0.17	0.029	0.022	SLAG I Casi Al
	4	1615	0.22	0.61	0.14	0.016	0.024	Gabiai
	5	1590	0.21	0.60	0.11	0.013	0.024	
	1	1600	0.25	0.72	0.18	0.032	0.022	
	2	1590	0.23	0.69	0.20	0.020	0.024	
V4	3	1600	0.23	0.68	0.29	0.017	0.023	
	4	1600	0.23	0.69	0.29	0.015	0.024	GabiAi
	5	1600	0.20	0.70	0.27	0.013	0.024	
	1	1580	0.28	0.68	0.30	0.033	0.018	
	2	1600	0.24	0.66	0.12	0.020	0.018	
V5	3	1600	0.23	0.63	0.20	0.013	0.018	SLAG II CaSiMa
	4	1600	0.22	0.62	0.21	0.012	0.019	Castiviy
	5	1610	0.22	0.61	0.18	0.012	0.018	

Note: Test 1- after melting; test 2-slag and 5 min blowing; test 3- after adding desulphurizes and 1 min purging; test 4- after 5 min of purging; test 5- after 10 min of purging

Malt	Chemical composition of slag (%)										
wen	SiO ₂	Al_2O_3	Fe_2O_3	TiO ₂	MnO	CaO	MgO	K_2O	Na ₂ O	B1	
V1	14.80	2.49	7.32	0.13	6.16	9.60	59.30	0.02	0.09	0.65	
V2	23.80	8.00	1.67	0.30	1.25	23.80	40.50	0.13	0.39	1.00	
V3	22.30	8.70	1.03	0.32	1.22	24.00	41.80	0.10	0.39	1.08	
V4	22.60	7.70	1.43	0.28	0.88	26.90	39.20	0.09	0.85	1.19	
V5	13.10	27.40	2.86	0.11	1.73	14.20	40.50	0.02	0.09	1.08	

Table 5. Chemical composition of slag

According to Table 5, increased amounts of MgO are observed. MgO is regularly present in basic slag and mostly comes from the

refractory lining. The content of total sulphur in slag by individual phases of the process is given in Table 6.

 Table 6. Total sulphur content in slag

Sample —	Total sulphur content in slag (%)									
	V1	V2	V3	V4	V5	V6				
1	0.04	0.02	0.02	-	0.05	0.03				
2	0.04	0.16	0.19	0.19	0.20	0.26				
3	0.01	0.10	0.07	0.19	0.16	0.12				
4	-	0.10	0.08	0.18	0.16	0.13				
5	-	0.10	0.09	0.15	-	0.11				

Data on the change of sulphur content by technological phases are shown in Figure 3. Figure 4 shows the initial and final sulphur content in low-carbon steel melts. The achieved desulphurization percentages of S are given in Figure 5, and the degree of desulphurization by individual technological phases is in Figure 6 Achieving a satisfactory degree of desulphurization has given input to the development of procedures for injecting powder reagents, usually based on compounds with Ca. By applying these procedures, the sulphur content can be reduced and deep desulphurization can be performed and the remaining sulphides and oxides are converted to a less harmful form.



Figure 3. Change in sulphur content by individual melts of low-carbon steel quality









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3. CONCLUSION

Practical research was realized in an induction furnace using basic refractory lining. The presented technology includes work in a protective argon atmosphere and the addition of strong desulphurizes (CaSiAl. CaSiMg).

The applied technology can effectively reduce sulphur in an induction furnace. The sulphur content in the metal, during the process, was reduced from 0.027-0.038% S to 0.012-0.013% S and the achieved average degree of desulphurization ranges from 56 to 66%.

The results of this research represent the contribution to the improvement of steel production technology from the aspect of desulphurization.

Conflicts of Interest

The authors declare no conflict of interest.

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