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PROVIDING ULTRA-LOW SULPHER CONTENT DURING OUT-OF-FURNACE TREATMENT OF STEEL

An effective method of steel desulfurization, which provides up to 0,002 ... 0,003% sulphur content reduction in the finished rolled steel products, has been developed. Partial removal of sulfur occurs in the furnace unit and ultra-low sulphur content is achieved by creating a high-basic refining slag during out-of-furnace steel treatment in the ladle-furnace unit. The proposed technological method improves quality indicators of the metal by regulated introduction of appropriate reagents (lime, fluorspar). It has been determined that additional introduction of silicocalcium wire into the steel at the end of the out-of-furnace treatment makes it possible to reduce sulfur content to 0.002%.

Keywords: *wire rod, nonmetallic inclusions, desulphurization, fluorspar, lime, argon.*

Introduction

One of the main tasks of metallurgical industry is carrying out constant studies of the possibilities to improve quality of steel, produced at minimal cost. Quality indicators of the metal depend on the degree of steel contamination with nonmetallic inclusions (NI) and on the content of harmful additives, particularly, sulphur [1 – 3]. Increased sulphur content causes development of red-brittleness during hot deformation of cast steel and is an indirect evidence of unsatisfactory deoxidation of the metal [4, 5]. NI degrade the quality of steel, because during hot and cold plastic deformation and in the use of finished products they can act as stress concentrators, which leads to premature failure of the metal. Steel contamination is regulated by normative documents [6]. Most of NI are deoxidation products. They are formed as individual separate or complex compounds during steel crystallization: oxides (FeO, CaO, MnO, Al_2O_3, SiO_2), sulfides (FeS; MnS), silicates ($FeO{\cdot}SiO_2$), nitrides (AlN, VN, TiN), carbides (VC, Fe_3C) and other types of inclusions [6]. Sulfides are located mainly at the boundaries of grains and their morphology depends on steel crystallization rate, the increase of which reduces their size and volume fraction due to slow diffusion near the grain boundaries during fast cooling of the metal. For carbon steels characteristic types of NI are oxides, silicates and sulfides [6]. Ensuring NI cleanliness of steel is an urgent problem for the metallurgists and researchers, engaged in obtaining qualitative assortment of steels, as increased metal contamination can negate all the efforts directed towards choosing rational chemical compositions and deformation-thermal treatment modes for the metals, particularly, for wire rods. Low concentration of sulfur in steel is the evidence of high metal deoxidation degree, which results in reduction of steel contamination with NI [4 – 6]. Technological production schemes, used in modern steelmaking units of mass production, do not make it possible to directly obtain steels with low ($S < 0.01$ %) and ultra-low ($S < 0.005$ %) sulfur content in the metal [7].

Numerous studies deal with various desulfurization methods [1, 3, 5]. However, only a few of them [6, 8, 9] consider steel behavior in relation to the definite stages of manufacturing process (steel-making unit → out-of-furnace treatment → rolled product manufacture), which determines relevance of the presented research.

Research aim is to improve the technology of steel manufacture and out-of-furnace treatment in order to achieve ultralow sulfur content in the wire rod.

Material and procedure of the research: high-carbon steel of C80D brand with chemical composition in accordance with the requirements of EN 16120-2:2011. The following equipment was used: spectrometers «ARL-3460», «Spectrolab-M», unit «Ströhlein Mat-6250» with sulfur analyzer (SA). The total amount of the wire rod, produced during investigations, was 2 640 tons.

Research results and discussion. The experiments were performed for steel melted in electric arc furnace (EAF), which is a part of the technological equipment of JSC 'Moldovan Metallurgical

Plant' (JSC 'MMP'). According to the plan of performing the experiments with the application of various technological schemes, a continuous cast billet with square section of 125×125 mm, made of steel S80D mm, was rolled into wire rod with the diameter of 5.5 mm. The metal is intended for producing high-strength cord wire with the diameter of 0.35 mm. According to the requirements of regulatory documents and technical agreements of different manufacturers with consumers, sulfur content in the rolled metal, intended for producing high-strength cold-deformed wire, should not exceed 0.003%.

Depending on the quality of charge materials, sulfur content in steel, melted in EAF, before discharge is 0.04 ... 0.05% on the average. Preliminary calculations showed that for achieving ultralow sulfur content in the finished steel total desulfurization degree (*Δ [S], %*) should be at least 92.5 ... 94.0%**.**

During melting of the charge and subsequent heating of the metal in EAF the temperature is relatively low, and the main task is oxidation of iron, manganese, silicon and phosphorus. At this stage the most important manufacturing operation is reduction of the phosphorus content and provision of partial desulfurization of steel. This is provided with lime additive and removal of P_2O_5 and CaS compounds into the slag.

According to the laws of thermodynamics, it is impossible to obtain ultralow sulfur content in the metal in furnace due to increased activity of oxygen in the metal and slag. Therefore, final desulfurization of steel is provided in the process of its secondary treatment in the ladle furnace unit (LFU) during deoxidation. Reduction of sulfur content in steel occurs due to introduction of sulfide-forming elements (calcium, manganese) and the subsequent withdrawal of NI into the slag. In this case NI removal degree is determined by composition and basicity of the slag. The maximum effect is achieved by creating high-basic refining slag ('white slag'), the main component of which is lime. NI removal occurs due to the upward flows of steel and their assimilation at the metal-slag interface and flotation of inclusions by CO bubbles during the reduction period of melting. The necessary condition in this case is bubbling of the metal bath and intensive steel blowing with argon. Table 1 presents data on sulfur content in steel by years at different manufacturing stages of metal production at JSC 'MMP'. The data indicate, that with the improvement of steel desulfurization technology, efficiency of the applied measures increased. Thus, in 1999 the total degree of steel desulphurization was 72.1% and sulfur content in the samples of metal, taken from the ladle tundish – 0.019% while in 2008 the achieved indicators were 92.5% and 0.003% respectively. First, removal of sulfur was carried out mainly during out-of-furnace treatment. However, mixing of metal and slag in LFU in the process of steel blowing with argon through the ladle bottom openings was insufficient and to obtain the required sulfur content, the process time had to be increased.

The presence of lime additive in EAF without introduction of fluorspar reduces steel desulfurization degree to 10%. With the introduction of CaF_2 in the amount of 0.33 kg / t the desulfurization degree increases to 45%, and if CaF_2 consumption is 1.42 kg / t – to 65%. Therefore, to increase effective reduction of sulfur content in steel, it is necessary to achieve the required fluidity of slag not only in the steelmaking unit, but in the process of out-of-furnace steel treatment in LFU, provided by regulated introduction of fluorspar.

Table 1

Changes of sulfur content in steel with improvement of the out-of-furnace treatment technology

Time period	Average sulfur content, % mass			Desulfurization degree at different stages of steel production, %		
	Place of sampling			EAF→LFU	LFU→IL	EAF→IL
	EAF	LFU	IL[1]			
1999	0.068	0.061	0.019	10.3	68.9	72.1
2002	0.073	0.059	0.015	19.2	74.6	79.5
2006	0.069	0.044	0.010	36.2	77.3	85.5
2008	0.058	0.036	0.008	37.9	77.8	86.2
2011	0.040	0.014	0.003	65.0	78.6	92.5

Note: 1 – intermediate ladle

Desulfurization degree at the output from EAF ($\Delta[S_{EAF}]$, %) and absolute reduction of sulfur content at the section EAF→IL ($\Delta[S_{EAF\text{-}IL}]$, %), depending on the consumption of CaF_2, is described by empirical relationships:

$$\Delta[S_{\text{EAF}}] = -107.8 \cdot G_{1CaF_2}^2 + 197.4 \cdot G_{1CaF_2} - 8.4 \quad (1)$$

$$\Delta[S_{\text{EAF-IL}}] = -1.47 \cdot G_{2CaF_2}^2 + 14.6 \cdot G_{2CaF_2} - 56.1 \quad (2)$$

where G_{1CaF_2} and G_{2CaF_2} – fluorspar consumption at the output from EAF and its total consumption respectively, kg/t.

According to the expressions (3) – (6), increased CaF_2 content leads to the reduction of viscosity and surface tension during out-of-furnace steel treatment in the ladle-furnace unit:

$$\eta_{(1)1500} = 0.4 - 0.018 \cdot [CaF_2] \quad (3)$$

$$\eta_{(2)1500} = 0.16 - 0.02 \cdot [CaF_2] \quad (4)$$

$$\sigma_{(1)1500} = 458 - 0.5 \cdot [CaF_2] \quad (5)$$

$$\sigma_{(2)1500} = 470 - 1.25 \cdot [CaF_2] \quad (6)$$

where $\eta_{(1)1500}$, $\eta_{(2)1500}$ – viscosity in the first and the last samples of slag in LFU, N.s / m^2; $\sigma_{(1)1500}$, $\sigma_{(2)1500}$ – surface tension in the first and last samples of slag respectively, MN / m.

The experiments have shown that the required metal desulfurization degree is obtained under complex influence achieved in the steelmaking unit and during out-of-furnace treatment of steel. The sequence of manufacturing operations is as follows: after steel is discharged from EAF into steel teeming ladle and furnace slag is completely removed, deoxidizing additives as well as regulated amounts of lime and fluorspar are introduced, metal treatment in LFU is performed, accompanied by argon blowing through bottom openings in the steel ladles.

Total consumption of fluorspar (G_{CaF_2}, kg / t) during steel desulfurization is determined from empirical dependence:

$$G_{CaF_2} = 0.292 \cdot \Delta S - 22.35 \pm 0.1 \quad (7)$$

Relationship between CaF_2 consumption in LFU ($G_{CaF_2}^{\kappa}$, kg / t) and its consumption at the output from LFU($G_{CaF_2}^{н}$, kg / t) should be 3:1.

The ratio $G_{CaF_2}^{\kappa} : G_{CaF_2}^{н} = 3:1$ provides the necessary sulfur content in the metal while the time and electric energy consumption, required for out-of-furnace treatment, are reduced (Table 2).

Table 2

Comparative analysis of technical-economic indices under regulated fluorspar consumption

Steel brand	$G^{\kappa}_{CaF_2} : G^{н}_{CaF_2}$	The time of out-of-furnace treatment, min	Electric energy consumption, KWh /t
C80D	2:1	55	48.5
	3:1	50	44.1
	4:1	50	44.3

As the ratio $G^{\kappa}_{CaF_2} : G^{н}_{CaF_2} = 4:1$ increases, the time of out-of-furnace treatment and electric energy consumption remain practically the same but, however, the desulfurization process is characterized by unjustified overconsumption of fluorspar.

For the first series of heats of steel C80D (880,0 t) the following consumption of reagents was adopted: fluospa – 4.7 kg / t, lime – 10.1 kg / t, silicocalcium wire (contains 40 % Ca) – 0.9 kg / t, argon – 4,2 l /t·min. The degree of steel desulfurization was 93.8 % and sulfur content in the finished steel – 0.0025 %. In the second series of heats total consumption of CaF_2 was reduced by 0.2 kg / t and total steel desulfurization degree reached 92,2 % with sulfur content in the finished steel – 0.0034 %. Although this sulfur content in the metal exceeds normalized value (maximum 0.003%), this deviation is permissible within the measurement error.

In the third series of heats the total fluorspar consumption was reduced to 3.0 kg / t. Desulfurization degree was 86.8 % with average sulfur content in the finished steel – 0.0052 %. In the last series of heats sulfur content in the metal was unacceptable in accordance with the requirements to high-quality wire rod made of high-carbon steels (specification «Pirelli» – «02.B.001.2», specification «Bekaert» – «GS-02-002»).

In this case, however, it should be understood that regulated introduction of CaF_2 is not so much determined by its influence on steel desulfurization degree, but rather by the necessity to increase fluidity of the high-basic refining slag (consisting mainly of *CaO*), capable of assimilating nonmetallic inclusions at the metal-slag interface, which contributes to achieving deep degree of steel desulfurization. Special attention should be paid to the influence of silicicalcium wire additive, which is introduced at the end of steel out-of-furnace treatment in LFU, when most of the sulfur is already removed. However, on the route from LFU to IL sulfur content is further reduced to ~ 0,002 % due to the additional influence of calcium. For ensuring guaranteed ultralow sulfur content in finished steel, at JSC "MMP" the following norms of the consumption of reagents were adopted (Table 3):

Table 3

Norms of lime and fluorspar consumption during high-carbon steel desulfurization

Name of material	Technological stage		Total
	At the output from LFU	In LFU	
CaF_2, (kg / t ±0,1)	1.18	3.55	4.73
CaO, (kg / t ± 0,1)	3.47	6.64	10.11
Ratio $CaF_2 : CaO$, %	0.34	0.53	0.47

The developed method establishes the sequence of technological operations, the type and consumption of reagents, which makes it possible to create a high-basic refining slag on the surface of metal, chemical composition and properties of which are the most favorable for achieving the required degree of steel desulfurization. Steel treatment with refining slags enables not only reduction of sulfur content in the metal, but also of steel contamination with NI (oxides, sulfides, silicates), which increases technological plasticity of the rolled steel at the cord production stage [9].

The method of deep desulfurization of steel was implemented at JSC "MMP" as a part of standard steelmaking equipment, but the research results can be used at metallurgical enterprises of Ukraine: PJSC "ArselorMittal Kryvyi Rih", PJSC "Dnieper Metallurgical Plant" and PJSC "Yenakiyevo branch of MakMP".

Conclusions

1. An efficient technology of steel desulfurization has been developed. The technology makes it possible to ensure sulfur content in the wire rod, which does not exceed 0.003 %. Sulfur is partially removed, when steel is discharged from the steel-melting unit, and a pre-determined steel desulfurization degree is provided by regulated introduction of lime and fluorspar, mostly in the process of out-of-furnace treatment.

2. The obtained empirical dependencies enable determination of steel desulfurization degree at the output of steel-melting unit and absolute reduction of sulfur content on the technological process route steelmaking unit → intermediate ladle → finished steel, depending on the total fluorspar consumption. It has been found that in order to achieve an ultralow sulfur content in wire rod due to the use of high-basic refining slag, the ratio of the amount of CaF_2 during out-of-furnace treatment and its amount, consumed at the output of steel-making unit, should be 3:1.

3. The proposed method of deep desulfurization of steel makes it possible to improve quality indicators of the wire rod. Ultralow sulfur content prevents development of cracks in the process of hot deformation of a cast billet (the phenomenon of red-brittleness), reduces total content of NI of oxide type in steel and, as a consequence, increases technological plasticity of wire rod during subsequent cold plastic deformation by drawing.

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