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CHANGE IN SLAG COMPOSITION AND SULFUR CONTENT OF HOT METAL IN THE PROCESS CHAIN OF BLAST FURNACE — HOT METAL DESULFURIZATION COMPLEX — CONVERTER (BOF)

Introduction. *Modern conditions of iron and steel making industry require production of high-quality competitive metal products. Thus, the removal of sulfur at the lowest cost has been becoming increasingly important.*

Problem Statement. *The major amount of sulfur in iron and steel making comes with charge materials in sintering blast furnace production. When using out-of-furnace processing of hot metal in hot metal desulfurization and slag removal facilities, the degree of hot metal desulfurization can be 75—99%. This ensures the production of hot metal with a sulfur content in the range of 0.002—0.015%.*

Purpose. *The analysis of changes in the sulfur content of hot metal and in the slag composition in the process chain of steel production, followed by the development of technical solutions and process methods to eliminate the resulfurization of hot metal.*

Materials and Methods. *Our calculations, based on the actual data of Ukrainian and Chinese iron and steel making facilities. The selected samples of slag and hot metal have been analyzed with the use of raster spectral microscopy methods. In the studies of sulfur content at various stages of smelting, the method of material balance calculation has been employed.*

Results. *In the slag phase, along with systems of* $CaO \cdot SiO_2 \cdot Al_2O_3$ *type with different ratios of components containing 0.2—3.5% sulfur,* $Ca_xSi_yAl_z$ *type systems containing up to 1% sulfur have been detected. In the beads, the sulfur content varies within 0.1—0.85%. Sulfur is present in the form of sulfides of (Fe, Mn)S type, mainly MnS, while in non-metallic inclusions of the beads, the sulfur content ranges within 15—30%. The residing ladle slag after desulfurization should not exceed 0.5—0.7 kg/t of hot metal.*

Conclusions. *To prevent the resulfurization of hot metal during its discharge from a blast furnace, it is advisable to rationalize ladle slag modes, by adjusting ladle slag composition, increasing the degree of ladle cleaning*

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from the slag residing from previous loads and inducing a slag cover in the absence of ladle slag. The conducted studies have shown that sulfur from the slag does not return to the hot metal and resulfurization does not occur, which is explained by the protective effect of residual magnesium.

Keywords: out-of-furnace desulfurization of hot metal, slag, sulfur, and resulfurization.

The problem of sulfur removal with the lowest costs has been becoming more and more important in the production of high-quality and competitive metal products [1—3].

The given paper analyzes changes in the sulfur content of hot metal and in the slag composition in the process chain of Blast Furnace — Hot Metal Desulfurization Facility — Oxygen Converter Facility (Fig. 1). Based on the research results, we have developed and recommended technical solutions and technological approaches for eliminating hot metal resulfurization. Our calculations [4—6], based on the actual data of Ukrainian and Chinese iron and steel making facilities.

DISCHARGE OF HOT METAL FROM BLAST FURNACES INTO LADLES

Studies [7—9, 12] of the chemical and phase compositions of blast-furnace and ladle slag carried out over the past four decades at various iron and steel making facilities in Ukraine, PRC, and Taiwan have shown that they differ significantly. This is due to the fact that ladle slag is the product of multifactorial formation. The composition of ladle slag depends on the amount of products of ladle lining destruction (mainly SiO_2) entering the ladle, ladle slag residues from previous hot metal portions, as well as on the amount of hot metal and manganese oxides formed from the oxidation of hot metal open surface on the chute and metal stream during the ladle filling. The basicity of ladle slag, as compared with that in the chute of blast furnaces, decreases from 1.08—1.27 to 0.17—0.63.

In ladle slags, the equilibrium distribution coefficient of sulfur is less than the actual one [6] and, therefore, the thermodynamic probability for the reverse transition of sulfur from slag to metal in these slags is quite high. Considering the presence of more favorable kinetic conditions when filling the hot metal car ladles, and as a result of a decrease in the sulfide capacity ($C_S = 7.9 \cdot 10^{-6}$—$6.3 \cdot 10^{-5}$) and basicity (0.17—0.63) of ladle slag, the necessary conditions for the reverse transition of sulfur from slag to hot metal may occur during the hot metal discharge from blast furnaces.

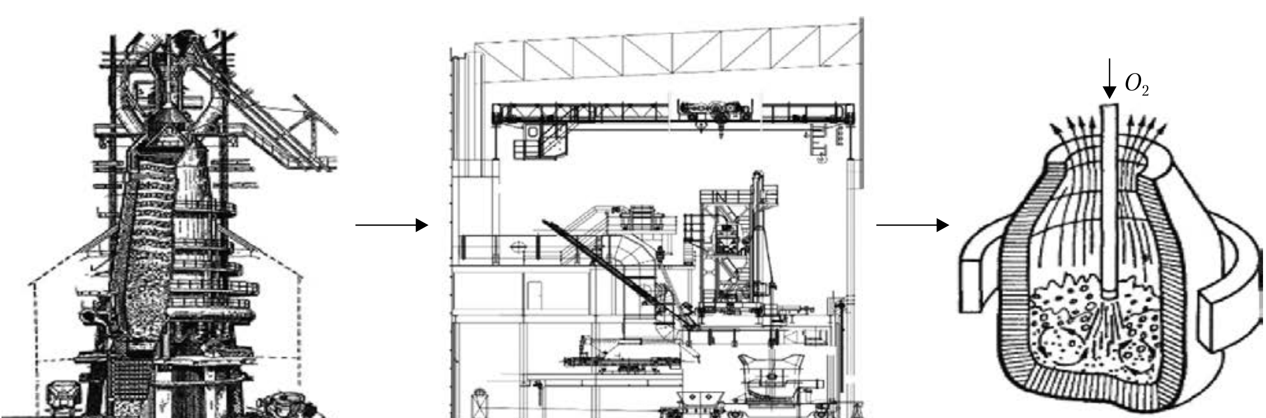


Fig. 1. Scheme process chain of Blast Furnace — Hot Metal Desulfurization Facility — Oxygen Converter Facility

In industrial practice, there are mainly dry, crumbly ladle slags with “islands” in the form of solid crusts. Liquid, vitreous slags are much less common. Dry, crumbly ladle slags are inactive in terms of interfacial diffusion redistribution of sulfur. Their activity increases during pouring hot metal from ladle to ladle, to mixer, and to pouring ladle, when the hot metal is intensively mixed with slag. As a result, specific reaction surface of the slag increases and its viscosity decreases because of heating. Such kinetic factors can contribute to hot metal resulfurization, especially at a low slag basicity (< 0.8).

Dry crumbly slags are a mix of metal (20—50%) in the form of beads, splashes, residues of cakes, slag (46—78%), and graphite (2.2—4.6%) in the form of flakes [7]. The share of beads in these slags is 30%, on average. In liquid slags, the share of beads ranges within 1.4—9.8% and is 4.8%, on average [9]. The basicity of ladle slags of both types varies widely (0.07—0.64) and averages 0.5.

The analysis of the slag bead structure by the optical microscopy and scanning electron microscopy methods has shown that they have a ferrite-graphite structure of a pre-eutetic or eutectic type with non-metallic inclusions in the form of manganese and hot metal sulfides [9]. The point probe scanning of ladle slag samples has shown:

- in the slag phase, there are detected $Ca_xSi_yAl_z$, type systems containing up to 1% sulfur along with systems of $CaO \cdot SiO_2 \cdot Al_2O_3$ type with different ratios of components containing 0.2—3.5% sulfur;
- in the beads, the sulfur content ranges from 0.1—0.85% and is in the form of sulfides of (Fe, Mn)S type, mainly MnS. In the non-metallic inclusions of the beads, sulfur content is within the range of 15—30% [9, 10].

Thus, beads similarly to slag, are the sources of sulfur influx to hot metal [7—10].

The studies at the Azovstal Iron and Steel Works, during 49 hot metal processing sessions (182 ladles) [7], have confirmed that hot metal resulfurization takes place during hot metal pouring into ladles. The sulfur content in hot metal car ladles after their filling in the blast-furnace facility was generally by 0.010—0.024% higher than in the blast-furnace chute. It has been found that as the amount of slag in the ladle increases, and the basicity and the sulfur content in hot metal decrease, the amount of sulfur transferred from slag to hot metal goes up.

The similar studies at the Azovstal Iron and Steel Works during 2020—2021 have shown a decrease in the amount of hot metal resulfurization that amounts to 0.003—0.010%, as a result of the use of concrete chutes, change in the technology of blast-furnace smelting, which reduces the sulfur content in hot metal, as well as due to a decrease in the amount of ladle slag.

Therefore, due to the resulfurization of hot metal in hot metal car ladles during hot metal discharge from blast furnaces, one should not be guided by the results of analysis of samples taken on the chutes of blast furnaces to assess the sulfur content in hot metal in hot metal car ladles.

To prevent the transition of sulfur from slag to hot metal, it is recommended to use correctional additives of CaO-based materials (including granular non-fractionated waste products from the production of metallurgical lime at a rate of 1.0—2.0 kg/t of hot metal) to increase the slag sulfide capacity.

The effect of correctional additives (granular non-fractionated waste products from the production of metallurgical lime) fed to the bottom of hot metal ladles at a rate of 1.0—2.0 kg per ton of hot metal prior to discharging hot metal from blast furnaces has been estimated on the site of Ukrainian Iron and Steel works [7]. The study has shown that an increase in the sulfur content in hot metal was reduced 1.5—2 times.

At Chinese Iron and Steel works (Qianyan Iron and Steel facility), feeding correctional additive (metallurgical ground powdered lime at a rate of 2—2.5 kg/t) to the bottom of pouring ladles before pouring hot metal into them from mixing ladles, has ensured a double reduction in the increase of sulfur content in hot metal.

OUT-OF-FURNACE HOT METAL DESULFURIZATION

Globally, there are used the three major technological processes of out-of-furnace hot metal desulfurization: monoinjection of dispersed magnesium, co-injection of CaO-Mg mix [8, 12—13], and KR-process (mechanical mixing of hot metal with lime and CaF_2 additive). The comparative technical and economic analysis of these hot metal desulfurization processes [9] has shown that magnesium monoinjection is the most efficient of them. In addition, the authors of [14] have indicated that lime injected with magnesium by the co-injection method into cast iron practically does not participate in the process of sulfur removal, so lime is only a filler when adding magnesium. Therefore, that research has investigated the process of injecting magnesium into hot metal. Hot metal desulfurization by magnesium monoinjection is characterised by the lowest specific reagent consumption, the lowest operating and capital costs, the smallest treatment cycle, the lowest losses of hot metal and its temperature, and the highest stability of the results achieved.

In this paper, we have studied the interfacial redistribution of sulfur in ladle slags during hot metal desulfurization by monoinjection of granular magnesium. During the research, we have investigated changes in the chemical composition of slags of the two types: dry and liquid. Based on the data in Table 1, it can be seen that the compositions of ladle slags of various hot metal and steel making facilities differ significantly.

At the facilities where the source ladle slags are dry and crumbly, after desulfurization, the sulfur content in them increases 1.3—15 times, the MgO content increases 1.5—8.5 times, and that of FeO grows 1.1—3 times. At the Yuanli Iron and Steel Works, where the initial slags are liquid and vitreous, the sulfur content after desulfurization increases 1.3—30 times (7.7 times, on average) while that of MgO goes up 1.1—2.1 times (1.7 times, on average).

The content of FeO and Fe_2O_3 in the ladle slag after desulfurization changes both upwards and downwards and, on average, decreases 1.35 and 1.42 times, respectively.

Table 1. **(Average) Characteristics of Ladle Slags Before (numerator) and After (denominator) Hot Metal Desulfurization by Magnesium at Various Companies**

Company	Sulfur content, %		Ratio $\frac{CaO}{SiO_2}$	Ratio $\frac{CaO + MgO + MnO}{SiO_2 + Al_2O_3}$	Ratio (S)/[S]	Slag type
	In hot metal	In slag				
Zaporizhstal (Ukraine)	$\frac{0.052}{0.024}$	$\frac{1.06}{3.53}$	$\frac{0.58}{0.62}$	$\frac{0.63}{0.94}$	$\frac{20.3}{147}$	Dry, crumbly
Illych Iron and Steel Works (Ukraine)	$\frac{0.038}{0.006}$	$\frac{1.43}{3.81}$	$\frac{0.84}{0.73}$	$\frac{0.99}{1.15}$	$\frac{37.6}{638}$	Dry, crumbly
Azovstal (Ukraine)	$\frac{0.026}{0.003}$	$\frac{0.80}{2.45}$	$\frac{0.54}{<1.0}$	$\frac{0.63}{<1.1}$	$\frac{30.8}{817}$	Dry, crumbly
Kryvoryzhstal (Ukraine)	$\frac{0.069}{0.019}$	$\frac{1.07}{5.89}$	$\frac{0.76}{0.71}$	$\frac{0.76}{1.05}$	$\frac{16.7}{414}$	Dry, crumbly
Xiangtan Iron and Steel Works (China)	$\frac{0.028}{0.005}$	$\frac{0.30}{0.65}$	$\frac{0.20}{0.22}$	$\frac{0.16}{0.21}$	$\frac{3.3}{98}$	Dry, crumbly
Handan Iron and Steel Works (China)	$\frac{0.018}{0.005}$	$\frac{0.31}{1.12}$	$\frac{0.36}{0.33}$	$\frac{0.29}{0.31}$	$\frac{17.3}{216}$	Dry, crumbly
Yuanli Iron and Steel Works (China)	$\frac{0.031}{0.019}$	$\frac{0.13}{1.00}$	$\frac{0.50}{0.40}$	$\frac{0.66}{0.69}$	$\frac{4.1}{52.6}$	Liquid

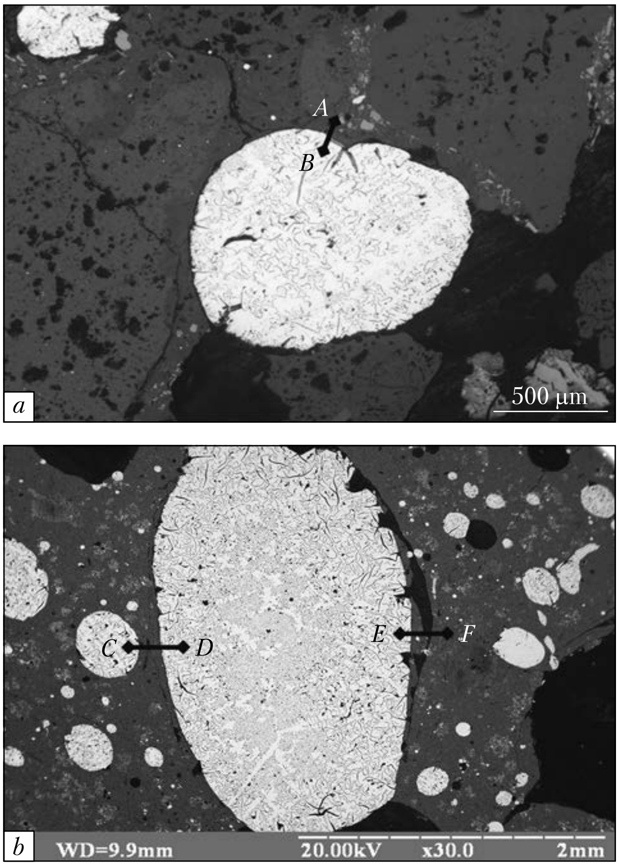


Fig. 2. Microstructure of metal and slag phases of the ladle slag samples taken before (*a*) and after (*b*) hot metal desulfurization with granulated magnesium

Point probe scanning route: *A—B, C—D, E—F.*

This is explained by the lower hot metal oxidation during the bubbling due to the coating of the metal surface with a layer of liquid slag, as well as because of the dilution of the slag composition due to the addition of sulfur and MgO to the slag.

The metal phase content in dry slag increases slightly by 5—7% abs. In liquid slags, the content of the metal phase increases 3.7 times, on average (up to 17.6% abs.).

The analysis of the sulfur content in slags before and after hot metal desulfurization (Table 1) with magnesium has shown that the change in the sulfur content in slags is basically affected by the amount of initial (before desulfurization) ladle slag and its basicity. It has been found that the greater the amount of sulfur transferred from the hot metal to the slag, the greater the amount of slag in the ladle, the higher the basicity of the initial slag, and the lower the sulfur content in the hot metal after desulfurization. At the same time, the basicity of CaO/SiO_2 slag does not fundamentally change, and the slag in the ladle remains acidic after desulfurization. When MgO influx to the slag is significant and the basicity of the slag $(CaO + MgO + MnO)/SiO_2 + Al_2O_3$ becomes greater than unity, the sulfur absorption capacity of the slag increases. An increase in the MgO content in slag is associated with increasing slag viscosity and melting point, by 40—60°, due to the formation of refractory compounds, such as forsterite ($2MgO \cdot SiO_2$) and monticellite ($CaO, MgO \cdot SiO_2$) [7].

The composition studies of dry, crumbly, and liquid vitreous ladle slags after desulfurization have shown that they do not change the phase composition, but, unlike the initial ladle slags, the slag phase of such slags mainly contains systems of the $CaO \cdot SiO_2 \cdot Al_2O_3 \cdot MgO$ type, enriched with magnesium oxides, with a variable ratio of components. At the same time, sulfur in the slag phase of dry slags is mainly in the form of complexes (Ca, Mn, Mg, Al, Si)S, while in the slag phase of liquid slags it is mainly in the form of MnS and less often in the form of complexes (Ca, Mn,)S. In both types of slag, the sulfur content is at the level of 2%, whereas for the slag components, the sulfur content reaches 16%. In addition, in the slags of both types, there have been found inclusions of Ca—Si—Al—Mg alloys with different ratios of components, containing 2—4% sulfur.

The analysis of the structure of slag beads after desulfurization [9] has shown that the structure almost does not change and corresponds to the structure of slag beads sampled before desulfurization, remaining the ferrite-graphite one that can be conditionally attributed to the hypoeutectic (in the case of the presence of developed dendrites of solid solution of the matrix phase, the ferrite) or the eutectic type, Fig. 2.

The analysis of patterns of interfacial distribution of sulfur during hot metal treatment by magnesium monoinjection [10, 11], using the data of experimental treatments under industrial conditions, has shown that almost the whole sulfur removed from the metal goes into the slag and metal (beaded) phases of the slag, where it is present in the form of Ca and Mn compounds. At the same time, there is a rapid transition of sulfur from the slag to the metal beads. The average sulfur content in the beads after desulfurization depends on their particle size composition and increases as the size of the beads grows. It has been found that while the metal-slag system is held for two hours, there is almost no transition of sulfur from slag to hot metal. It is limited to the diffusion of sulfur in the slag.

The studies have shown that ladle slags have a significant effect on the interfacial distribution of sulfur in the process of hot metal desulfurization with injected magnesium and have wide physicochemical characteristics.

When developing technological processes for specific initial conditions, one should take into account the influence of ladle slags and, if necessary, provide for technological methods that exclude the negative impact of ladle slags on the efficiency of hot metal desulfurization. In order to make ladle slag regimes feasible, it is recommended:

- to improve the degree of hot metal car ladle cleaning from the remains of ladle slag from previous portions;
- if necessary, to adjust the composition of ladle slags (before and after out-of-furnace treatment with various reagents), including the use of non-fractionated waste metallurgical lime, waste refractory materials, and dry crushed (granulated) blast-furnace slags;
- in the absence of a slag cover, it is advisable to induce it, for example, using non-fractionated waste products of metallurgical lime at a rate of 1.0—1.5 kg per 1 ton of hot metal.

The estimate of the costs of desulfurization and slag skimming in the facilities of out-of-furnace treatment of hot metal by magnesium monoinjection has shown that they are significantly lower than those in blast-furnace production. As the sulfur content in hot metal decreases from 0.055% to 0.025%, the specific costs in the facilities for hot metal desulfurization by magnesium monoinjection are ~USD 0.9 /t · 0.01%ΔS.

TRANSPORTATION OF LADLES WITH DESULFURIZED HOT METAL

The studies at Azovstal Iron and Steel Works (Ukraine) [9], when transporting desulfurized hot metal with magnesium in open blast-furnace ladles from the hot metal desulfurization department to the slag skimming department have shown that there are no significant changes in the sulfur content in hot metal. Out of the 49 controlled ladles with desulfurized hot metal, the sulfur content was lower by 0.001—0.002 abs. % in 14 ladles, after 0.7—2.7 hours, in 14 ladles it was higher by 0.001—0.002 abs. %, while in 21 ladles the sulfur content did not change. The deviations were within the accuracy of express analysis (±0.002 abs. %).

Despite the existing thermodynamic possibility, resulfurization in ladles with the desulfurized hot metal, which are characterized by an order of magnitude higher excess of the actual sulfur distribution coefficient over the equilibrium one ($\Delta L_S \geqslant 120$), as compared with the non-desulfurized hot metal, the return of sulfur from slag to hot metal has not been reported. This is due to the two factors. Firstly, because of the lack of proper kinetic conditions in hot metal ladles. Secondly, because of the presence of residual magnesium in the desulfurized hot metal, which has a protective effect over the resulfurization process. The magnesium that remains in the hot metal in an amount of ⩾ 0.005% has been found to create a protective barrier, preventing the return of sulfur from the ladle slag to hot metal.

POURING OF DESULFURIZED HOT METAL FROM LADLES TO MIXERS

In the case of the desulfurized hot metal, there are more favorable thermodynamic conditions for hot metal resulfurization than those when pouring

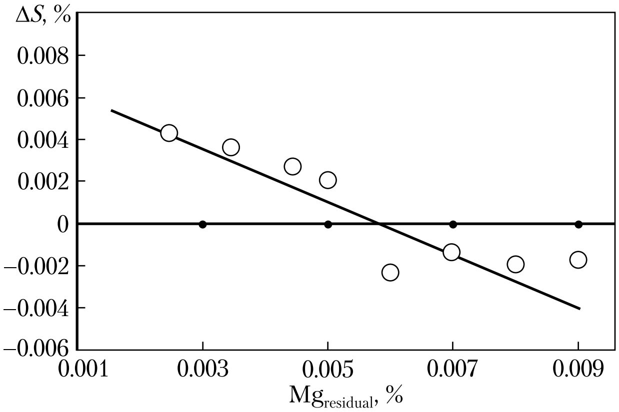
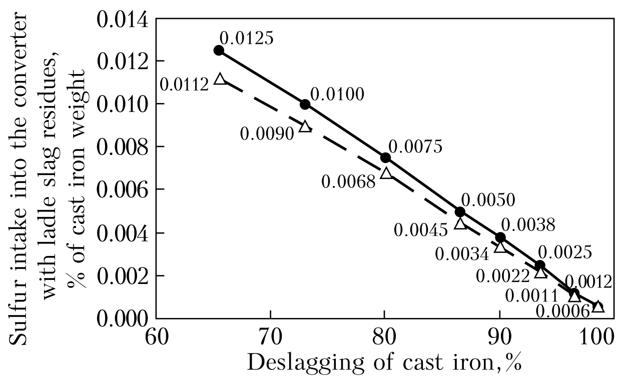


Fig. 3. Dependence of the change in the sulfur content (ΔS) on the content of residual magnesium (Mg_{res}) in hot metal when it is poured from a mixer or a blast ladle into a pouring ladle



The numbers near the dots are the values of sulfur influx to the converter with slag.
The final sulfur content in hot metal is 0.002%.
—●— injection of granular magnesium;
—△— injection of magnesium mixed with lime.

Fig. 4. Dependence of sulfur influx into the converter bath (with residues of ladle slag) on the degree of slag removal from the ladle after desulfurization

non-desulfurized hot metal [9]. The studies at the Azovstal Iron and Steel Works have shown that the excess of the actual sulfur distribution coefficient over the equilibrium one when transferring deep-sulfurized hot metal with an average sulfur content of 0.0025% to the mixer is ΔL_S = 80—375. Despite this, the sulfur does not return from slag to hot metal. Moreover, there is a decrease in the sulfur content in hot metal poured into the pouring ladle by an average of 0.0005%. The lack of hot metal resulfurization is explained by the protective effect of residual magnesium. The reported decrease in the sulfur content in hot metal is associated with the completion of the ongoing desulfurization processes between magnesium and sulfur dissolved in hot metal and the formation of magnesium sulfides in the slag phase.

Based on the results of on-site experiments, a relationship between the magnesium content in desulfurized hot metal and the change in the sulfur content while holding the hot metal in the mixer (Fig. 3) has been established. The magnesium content of in hot metal, which exceeds 0.006—0.008%, not only prevents the return of sulfur to hot metal, but also has some desulfurizing effect on the metal.

Also, it has been found that during all operations with deeply desulfurized hot metal (including its transportation and pouring from hot metal ladles to a mixer and from a mixer to pouring ladles), the sulfur content in hot metal remains unchanged. At the same time, there has been a decrease in the content of residual magnesium from 0.038—0.040% (in hot metal of hot metal ladles) to 0.017—0.020% (in hot metal of pouring ladles).

The long-term industrial experience of Ilyich (9 months) and Azovstal (more than two years) Iron and Steel Works with the provision of sulfur content in hot metal in mixers ⩽ 0.005% has confirmed that the presence of residual magnesium in magnesium-desulfurized hot metal is a significant factor that reliably excludes the return sulfur to hot metal.

HOT METAL TREATMENT FROM LADLE SLAG

The presence of high-sulfur ladle slag in the non-desulfurized hot metal and especially in the desulfurized hot metal, in which the sulfur content is even higher, determines the importance and necessity of effective ladle slag removal from hot metal (Fig. 4), since in the converter smelting, sulfur supplied with ladle slag can be transferred into metal. At the same time, the possibilities of removing sulfur in the converter bath are very limited.

To increase the efficiency of the treatment of hot metal from ladle slag, to reduce hot metal losses during the slag removal and to shorten the duration of the hot metal purification, the following technological methods have been used, including:

- nitrogen injection into hot metal during slag skimming, which ensures the movement of the slag mass to the zone of its removal from the ladle by the slag skimmer;
- adjusting the slag composition with thickening and diluting additives (for example, non-fractionated waste of metallurgical lime, dry crushed (granulated) blast-furnace slag).

Slotted refractory inserts in the bottom of the ladle, as well as bubblers with submersible refractory lances have been used to purge hot metal with nitrogen.

To remove slag from ladles, most advanced scraper-type skimmers manufactured by *Gerwin Holtmann* (Germany), *Dango Dienenthal* (Germany), and the Tangshan Machine Plant (PRC) are recommended.

Based on the results of on-site experiments at many enterprises in Ukraine and PRC, it has been found that in order to limit the influx of sulfur into converter steel with slag at a level of ⩽ 0.002%, the residue of ladle slag after desulfurization should not exceed 0.5—0.7 kg/t of hot metal.

STEEL SMELTING IN CONVERTERS

The determining factors for sulfur influx into converter steel are as follows: the sulfur content in the charge materials, primarily in the used scrap and iron, as well as the degree of purification of hot metal from high-sulfur slag. Since the capabilities of metal desulfurization in the converter are limited and the costs of metal desulfurization increase due to the deterioration of the indicators of the converter stage, for the smelting of extra-pure steel grades, there are used the desulfurized hot metal refined to a sulfur content corresponding to the level in the steel that is being smelted and the scrap with a similar sulfur content (usually trimmings from the rolling production of steels of the same assortment). In the absence of scrap of the required assortment, extra-pure steels can be smelted with the use of desulfurized hot metal and pellets.

Experimental studies of the sulfur influx into steel during the smelting of ultra-pure steels in converters using deep desulfurized hot metal have been carried out at 300-ton converters of the Azovstal Iron and Steel Works and Steel Making Facility No. 3 of Wuhan Iron and Steel Works, China. The data characterizing the initial conditions of the experiments and the results obtained are shown in Table 2. Metallized pellets (89.46—90.28% Fe_{met}, 1.36—1.71% C, 0.006% P, 1.36—1.55% CaO, and 0.003—0.004% S), as well as double slag skimming (from blast-furnace and pouring ladles) and draining almost completely slag-free hot metal into the converter have been used.

The analysis of the results obtained in the series of experimental smelts in 300-ton converters with the use of pellets has shown that the sulfur influx to steel in all five treatments is lower than the designed one (according to the balance) by 0.00002—0.00165%. The established error can be considered quite acceptable for industrial experiments. The results obtained on the sulfur balance have shown that in converter smelts at the Azovstal Iron and Steel Works, the degree of metal desulfurization is ~7%, while at the Wuhan Iron and Steel Works, it is ~3%. The identified conditional sulfur influx into steel corresponds to the level of sulfur influx into steel from charge materials and from ladle slag. At the same time, at the Azovstal Iron and Steel Works, where the slag was removed from the pouring ladles with exceptional care, the conditional sulfur influx into steel was 0.001—0.002% and associated with the influx of sulfur into steel from other charge materials. At Wuhan Iron and Steel Works, where hot metal was not thoroughly purified from slag, the conditional sulfur influx into steel was 0.005—0.009% and mainly associated with the influx of sulfur into steel from ladle slag.

Table 2. **Data Characterizing the Experimental Steel Smelting in 300-Ton Converters with Sulfur Balance Control**

Parameters	Azovastal Iron and Steel Works, Ukraine		Steel Making Facility No. 3 of Wuhan Iron and Steel Works, China		
	Tags of the smelts				
	2004329	2004401	531275	531279	531350
1. Hot metal characteristics:					
1.1. Hot metal mass, t	308	294	278	278	278
1.2. Sulfur content in hot metal, %	0.002	0.002	0.003	0.003	0.004
1.3. Hot metal temperature, °C	1365	1250	n/a	n/a	n/a
2. Ladle slag characteristics					
2.1. Slag mass, t	0	0	0.56	1.12	0.56
2.2. Sulfur content in slag, %	0.79	0.5	1.01	1.21	0.46
3. Material consumption per converter smelting					
3.1. lime:					
mass, t	36.0	23.0	14.335	17.0	12.93
sulfur content, %	0.017	0.017	0.025	0.025	0.025
3.2. Dolomite:					
mass, t	—	—	3.08	3.09	4.621
sulfur content, %	—	—	0.018	0.018	0.018
3.3. Pellets:					
mass, t	55.0	65.0	6.70	11.48	13.847
sulfur content, %	0.003	0.003	0.045	0.045	0.045
3.4. Fluorspar:					
mass, t	0	2.4	—	—	—
sulfur content, %	n/a	n/a	—	—	—
3.5. Oxygen, m^3	19900	20480	22080	15200	14880
4. Steel characteristics:					
4.1. Steel mass, t	286	273	256	256	256
4.2. Steel grade	09G2S	09G2S	n/a	n/a	n/a
4.3. Sulfur content in steel, %	0.004	0.003	0.008	0.012	0.008
4.4.Steel temperature, °C	1760	1670	n/a	n/a	n/a
5. Converter slag characteristics					
5.1. Slag mass, t	22.880	21.840	20.480	20.480	20.480
5.2. Sulfur content in slag, %	0.004	0.004	0.003	0.004	0.003
6. Design mass of sulfur taken to the converter, incl.:					
with hot metal, kg	6.16	5.88	8.34	8.34	11.12
with ladle slag, kg	0	0	5.66	13.6	2.58
with lime, kg	6.12	5.75	3.58	4.25	3.23
with dolomite, kg	—	—	0.55	0.56	0.83

End of Table 2

Parameters	Azovastal Iron and Steel Works, Ukraine		Steel Making Facility No. 3 of Wuhan Iron and Steel Works, China		
	Tags of the smelts				
	2004329	2004401	531275	531279	531350
with pellets, kg	1.65	1.95	3.01	5.16	6.23
total	13.93	13.58	21.14	31.91	23.99
7. Sulfur per ton of steel, %	0.00487	0.00497	0.00826	0.01247	0.0094
8. Amount of sulfur removed with slag during converter smelting per ton of steel, %	0.00032	0.00032	0.00024	0.0003	0.00024
9. Sulfur unbalance per ton of steel, %	–0.00055	–0.00165	–0.00002	–0.00017	–0.0012
10. Unrecorded sulfur influx to steel, $[S]_{st.} - [S]_{hm}$ %	+0.002	+0.001	+0.005	+0.009	+0.005

The experimental smelts have confirmed the predicted effect of ladle slag on the influx of sulfur into the converter and shown the need for careful removal of ladle slag. After Wuhan Iron and Steel Works achieved the degree of hot metal treatment from slag to ~95%, the sulfur content in converter steel with slag decreased to ⩽ 0.002%.

The impact of hot metal desulfurization depth in converters on the indicators of the converter stage has been assessed with the use of data from one of the Ukrainian iron and steel works.

It has been shown that when using hot metal with a sulfur content of 0.055% and smelting steel with a sulfur content of 0.025%, the lime consumption increases by ~21 kg/t, the converter rate decreases by ~12%, the consumption of metal charge increases by ~40 kg/t, that of ferromanganese increases by ~1.4 kg/t, that of refractories grows by ~0.14 kg/t, and the oxygen consumption goes up by 15 m^3/t, while the yield decreases by ~3%. At the same time, the specific costs associated with a decrease in the sulfur content in the metal in the considered range are ~USD 5.3 /t $\cdot$ 0.01%ΔS.

To improve the efficiency of sulfur removal, it is important, along with ensuring technologically and economically justified removal of sulfur at each metallurgical stage, to prevent the return of sulfur in the course of technological operations associated with hot metal pouring and its transportation. Pouring ladles are the most preferred place for out-of-furnace desulfurization of hot metal from the standpoint of resulfurization prevention.

To prevent the resulfurization of hot metal during its discharge from a blast furnace, it is advisable to rationalize ladle slag regimes, by adjusting the ladle slag composition, increasing the degree of ladle cleaning from the slag residing from previous loads, and inducing a slag cover in the absence of ladle slag.

To reduce the conditional sulfur influx during the converter stage, it is necessary to ensure thorough removal of slag from the surface of the hot metal before pouring it into the converter, limiting the residual amount of ladle slag to a level of at most 0.5—0.7 kg/t.

The comparison of the costs for reducing the sulfur content in Blast Furnace — Hot Metal Desulfurization Facility — Oxygen Converter Facility process chain has shown that the lowest specific production costs for desulfurization are reported for out-of-furnace desulfurization of hot metal.

Thus, the conducted studies have shown, and the long-term industrial experience has confirmed, that in all operations with deeply desulfurized hot metal obtained by magnesium mono-injection, no sulfur returns from the slag there is no to the hot metal and there is no resulfurization, which is explained by the protective effect of residual magnesium.

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ЗМІНА СКЛАДУ ШЛАКУ І ВМІСТУ СІРКИ В ЧАВУНІ У ТЕХНОЛОГІЧНОМУ ЛАНЦЮГУ ДОМЕННА ПІЧ — КОМПЛЕКС ДЕСУЛЬФУРАЦІЇ ЧАВУНУ — КОНВЕРТЕР

Вступ. У сучасних умовах виробництва металопродукції в чорній металургії, що характеризуються необхідністю виробництва високоякісного конкурентоздатного товару, питання видалення сірки з найменшими витратами набуває все більшої актуальності.

Проблематика. Значна кількість сірки при виробництві металопродукції надходить із шихтовими матеріалами в аглодоменному виробництві. При застосуванні позапічної обробки чавуну в комплексах десульфурації чавуну та скачування шлаку (КДЧ) ступінь десульфурації чавуну може складати 75—99 % і забезпечує отримання чавуну з вмістом сірки в межах 0,002—0,015 %.

Мета. Аналіз зміни вмісту сірки в чавуні та складу шлаку в технологічному ланцюгу виробництва сталі з подальшою розробкою технічних рішень та технологічних прийомів, спрямованих на виключення ресульфурації чавуну.

Матеріали й методи. Розрахунки, що засновані на фактичних даних роботи металургійних комбінатів України та Китаю. Відібрані проби шлаку та чавуну аналізували за допомогою методів растрової спектральної мікроскопії. При дослідженнях вмісту сірки на різних етапах переділів використовували методику розрахунку матеріального балансу.

Результати. У шлаковій фазі поряд із системами типу $CaO \cdot SiO_2 \cdot Al_2O_3$ з різним співвідношенням компонентів, що містять 0,2—3,5 % сірки, виявлені системи типу $Ca_xSi_yAl_z$, які містять до 1 % сірки; у «корольках» вміст сірки коливається не більше 0,1—0,85 % у вигляді сульфідів типу (Fe, Mn)S, переважно MnS, причому у неметалевих включеннях «корольків» виявлено вміст сірки не більше 15—30 %. Залишок ковшового шлаку після десульфурації не повинен перевищувати 0,5—0,7 кг/т чавуну.

Висновки. Для запобігання ресульфурації чавуну під час випуску його з доменної печі доцільно раціоналізувати ковшові шлакові режими, зокрема й за рахунок коригування складів ковшових шлаків, підвищення ступеня очищення ковшів від залишків шлаку попереднього наливу, наведення шлакового покриву у разі відсутності ковшового шлаку. Проведені дослідження показали, що сірка зі шлаку в чавун не повертається і ресульфурація не відбувається, що пояснюється захисною дією залишкового магнію.

Ключові слова: позапічна десульфурація чавуну, шлак, сірка, ресульфурація.