

Conference Paper

Unit Ladle-Furnace: Slag Forming Conditions and Stabilization

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Nowadays almost all smelted steel is processed in "ladle-furnace" (LF), where the steel is processed under refining conditions and brought to the desired temperature and chemical composition. Therefore, large amounts of refining slag are formed. Only in Russia there is about 1.4 million tons of slag exported to dumps annually. This slag cannot be processed by the schemes implemented in the industry, since the slag quickly turns into the tiniest dust during solidification and cooling. Such dust is easily aerated and carried by the wind for long distances; it pollutes soils, dissolves in ground, sedimentary and sewage waters. It also pollutes slag dumps that are suitable for processing for crushed stone.

According to the data [1], the main reason of the LF slag disintegration is the polymorphic transformation of dicalcium silicate ($2\text{CaO}\cdot\text{SiO}_2$, C_2S) (Figure 1), which is promoted by the high content of CaO in the slag. The high-temperature β -modification is converted to a low-temperature γ -modification, with an increase in volume by 12%, which causes internal stresses in the mass of monolithic slag and also causes slag disintegration. It is noted that even a small amount of $\gamma\text{-C}_2\text{S}$ (about 4 wt.%) may be enough for decomposition.

It is noted [1–5] that there are 4 ways to prevent the slag decomposition:

1. The slag quenching ($\beta\text{-C}_2\text{S}$ receives the ability to maintain its qualities in the temperature range from 25 to 700°C);
2. The borate addition (a partial substitution of SiO_4^{4-} ions in the C_2S structure by BO_3^{3-} ions, which prevent the transformation of $\beta\text{-C}_2\text{S}$ into $\gamma\text{-C}_2\text{S}$);

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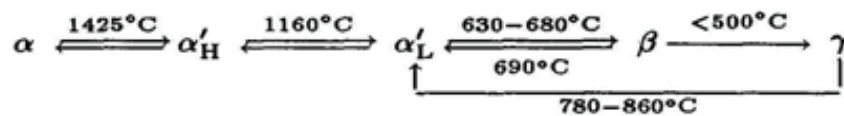


Figure 1: Scheme of dicalcium silicate polymorphism. H – high-temperature, L – low-temperature forms.

3. The non-borate stabilization based on the isomorphous substitution of Ca^{2+} ions by Mg^{2+} , K^+ , Ba^{2+} , Cr^{3+} , Mn^{2+} and SiO_4^{4-} ions by SO_4^{2-} and PO_4^{3-} ;
4. The slag phase composition control by chemical compounds addition that exclude the C_2S formation.

Each of these methods has its own drawbacks, preventing them from being widely introduced into production. We propose a combined approach for the stabilization of the LF slag by non-borate and chemical methods.

Initially, industrial LF slags of following enterprises were analyzed: JSC NSMMZ (Revda, Sverdlovsk region); JSC MMP (Magnitogorsk, Chelyabinsk region); JSC "MP after A. K. Serov" (Serov, Sverdlovsk region); JSC EVRAZ NTMP (Nizhny Tagil, Sverdlovsk Region); JSC Izhstal (Izhevsk). Each analysis included a calculated estimation of homogeneity and viscosity, an experimental evaluation of viscosity, and a qualitative analysis of the slag phase composition.

Calculations were made by the polymer model of slag structure. The heterogeneity of the slags and the amount of undissolved phase was determined from a comparison of components activity in a slag at a given chemical composition and temperature with the saturation activity values of these components at the same temperatures. The slag viscosity was measured on the vibrational viscometer.

Calculated and experimental data of viscosity and heterogeneity is presented in Table 1. For comparison, the table lists slags with JSC NSMMP (No. 1), JSC MMP (No. 2), JSC EVRAZ NTMP (No. 3 and 4). Taking the slag heterogeneity into consideration in calculations allowed the approximation of theoretical data to experimental data. The remaining inconsistency can be attributed by a simplified approach to the role of amphoteric oxides (for example Al_2O_3) in existing models. It can be noted from the data that industrial slags are often heterogeneous (amount of not dissolved phase from 0-2 mass% to 30-35 mass%) and have a sufficiently high viscosity (from 0.1 Pa.sec to 0.7-1 Pa.sec and even more). The phase composition analysis of slags showed a significant heterogeneity during cooling and solidification processes. The test results demonstrate the irrational slag management, which can affect the speed of metal processing in a ladle-furnace and the uniformity of components distribution introduced into the metal. In addition, the slag melt heterogeneity does not provide an effective implication

Slag number		1	2	3	4		
Component [wt.%]	Al ₂ O ₃	6,86	14,64	20,29	22,63		
	FeO	1,12	8,06	0,66	0,15		
	MnO	0,24	3,71	0,36	0,46		
	MgO	8,27	8,89	7,64	4,89		
	CaO	58,07	50,39	52,66	59,07		
	SiO ₂	24,45	14,32	18,39	12,8		
Viscosity [Pa.sec]	calculated	without taking into consideration the slag heterogeneity		0,051	0,077	0,145	0,157
		taking into consideration the slag heterogeneity		0,06	0,112	0,145	0,235
	measured	0,093	0,196	0,228	0,382		
Quantity of solid phases [wt. %]		3,5	8,89	0	8,8		
Slag heating temperatures before measurement [°C]		1580	1600	1550	1600		

TABLE 1: Viscosity and heterogeneity of industrial slags.

of each slag stabilization method. Therefore, it is advisable to provide refining slags stabilization by several methods at once.

For this purpose, it is proposed to use secondary aluminum production wastes (SAPW) (dispersed slag dust and waste from a crushing and concentration unit). The SAPW landfills can significantly decrease the ecological situation. The dispersity of SAPW allows us to control the obtained flux composition and briquetting parameters for suitable flux production in terms of chemical composition, size and strength characteristics. Secondary aluminum production wastes are based on the Al₂O₃ (up to 80 wt.%) and contain up to 12 wt.% of metallic Al. SAPW also contains up to 10 wt.% MgO, some SiO₂, CaO, Na₂O, K₂O, MnO and FeO. The presence of finely dispersed metallic aluminum in the flux composition will positively affect the metal and slag deoxidation. The Na₂O and K₂O oxides will provide the viscosity reducing of refining slag and prevent its decomposition.

To assess the effect of the proposed material on physical and technological characteristics of the slag, studies were made. They included calculating and measurement of viscosity, slag desulfurizing properties, and its surface tension [6]. The introduction of flux increased the liquidity of slags, increased their surface tension, which should positively affect the removal of nonmetallic inclusions from the metal to the slag. Desulfurizing properties was not decreased.

The next step was to determine limits of flux introduction into refining slags. Since the basis of the flux is amphoteric oxide Al₂O₃, the upper limit of flux introduction was the Al₂O₃ content in the slag, at which it begins to display behavior of predominantly acidic oxide. To determine this boundary, we have analyzed the diagrams of the

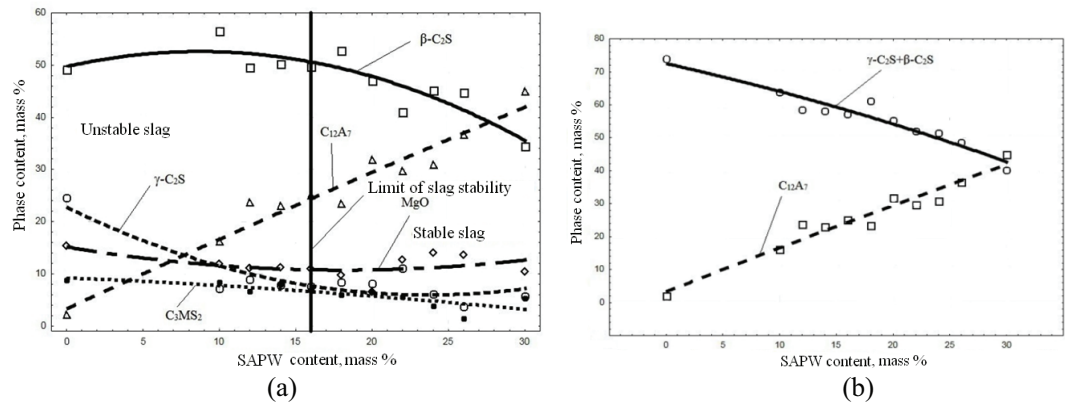


Figure 2: Quantitative phase content in the samples of model slag (a) and synthesized C₂S (b) with the addition of flux based on SAPW.

structure-sensitive properties by the polymer theory of the slag structure. It has been proved that Al₂O₃ shows predominantly acidic properties with a slag content more than 25-30 wt. % which impair slag technological properties and will adversely affect the quality of processed metal. When Al₂O₃ content in slag is up to 15-18 wt.%, the oxide shows predominantly basic properties, improving slag technological characteristics.

The lower limit of flux introduction was the Al₂O₃ content that allows preventing slag decomposition. The experiments showed that the stabilization of refining slags occurs with Al₂O₃ content higher 18 wt. %, while the refining slag and pure C₂S in parallel provided the determination of stabilization mechanisms (Figure 2). Stabilization of refining slag is predominantly chemical (12CaO·7Al₂O₃ (C₁₂A₇) is formed instead of γ -C₂S). Stabilization of pure C₂S is equally driven by chemical (with the formation of 2CaO·Al₂O₃·SiO₂ (C₂AS)) and non-borate (with β -C₂S retained instead of γ -C₂S) methods.

Since Al₂O₃ shows predominantly basic properties when its content in the refining slag is below 15 wt.%, it has been made an attempt to reduce the necessary for stabilization flux amount. Soda (Na₂CO₃) was introduced into the flux. Sufficiently 10 wt.% of soda from the mass of the flux was sufficient.

Since ladle furnaces use electric arc heating, we checked the effect of the developed flux on the electric arcs combustion regime [7]. Parameters which characterize the valve effect of burning arcs were chosen as evaluation criteria. Studies of the electric regime on a single-phase arc furnace made it possible to reveal a tendency of the parameters decrease with an increase of Al₂O₃ content up to 18 wt. % with further increasing. It allowed the data confirmation of Al₂O₃ acid-base properties. Obtained data in the electrical resistivity study of experimental slags with flux also confirmed the conclusions about boundaries Al₂O₃ acid-base properties in refining slags.

Industrial tests of the flux were carried out at following enterprises: JSC MMP (Magnitogorsk, at the stage of steel vacuum processing); CJSC MRC (Magnitogorsk) and JSC SPSNFM (Sukhoi Log) (during the recovery phase of smelting in an arc furnace); JSC NSMMP (Revda, at the stage of out-of-furnace steel processing in LF). To carry out the tests, LLC "SEAL and C" produced pilot batches of fluxes, according to the developed technical conditions.

The tests at the stage of steel vacuum processing were carried out with the o8ps steel. It has been noted that it is possible to completely replace fluorspar with the developed flux providing the required liquidity of the slag and removing the nonmetallic inclusions in the steel at the same time. In addition, the MgO content with flux in the slag increases to 8-9 wt. %, which positively affect the stability of the vacuum lining. There also was a decrease in the oxidation of the slag provided by the presence of aluminum metal in the flux composition.

Tests in the recovery phase of melting steel were carried out during the smelting of foundry grades of steel in an arc furnace. The effects of fluorspar substitution and simultaneous significant reduction of MnO and FeO in the metal were reached due to metallic aluminum in the developed flux. The economic effect of flux implication was reached due to the saving of aluminum concentrate and replacement of fluorspar.

The tests at the metal processing stage on ladle furnace were the main ones. The test results prove the possibility of completely fluorspar substitution with a developed flux, albeit not on all steel grades. The flux showed a good deoxidizing ability which reduced the consumption of ferroalloys and deoxidizers. Decreasing of the slag refining properties was not observed. Flux provides reliable stabilization of slags. The selected sample of experimental slags is suitable for the production of construction rubble according to the construction laboratory conclusion, which meets the normative requirements. In addition, technical specifications for the additive with an additional slag stabilizer were developed jointly with LLC "Seal and K".

The developed flux promotes import substitution in the metallurgical industry, since it allows replacing fluorspar which is scarce imported material. In addition, it reduces the consumption of ferroalloys and deoxidizers, reduces the cost of steel production. It provides the stabilization of refining slags and their further processing into a suitable commercial crushed stone. Solving the utilization issue of self-disintegrating refining slags and returning to the production of SAPW instead of its storage in dumps can reduce the environmental stress.

The work was carried out according to the State task "Processing of man-made waste (steelmaking slags) by pyrometallurgical methods with the aim of expanding the raw (or resource) base in ferrous metallurgy and construction branches, improving the quality and reducing the cost of metal products" (№ 0396-2015-0083).

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