UDC 669.168:669.017.12/13

Analysis of Refining Processes in Steel Ladle Treatment

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Developed resource-saving technology of steel treatment by metallic and slag-flux additives with the use of flux cored wires, synthetic alloys and solid slag mixtures from secondary raw materials allows raising technological efficiency of steel out-of-furnace treatment in 1.5-2.0 times.

Keywords: STEEL LADLE TREATMENT, SLAG, ADDITIVES, REFINING, NONMETALLIC INCLUSIONS

Introduction

The basic technological operations of iron-carbon melts refining such as deoxidation and sulfur removal are evaluated from thermodynamic characteristics of chemical reactions in equilibrium conditions in the metallurgical process theory. However, the metallurgical processes take place under nonequilibrium conditions as the systems are open and there is power and substance interchange with environmental, i.e. chemical reactions are irreversible and numerical values of equilibrium constant become conventional.

At present, metallurgical systems are referred to stochastic ones [1, 2], in which the processes progress under probabilistic laws that allow creating a consecutive series of chemical reactions to explain the certain stages of refining mechanism and defining consumption coefficients of additives (reduction alloys, ferroalloys, etc.) and amount of refining products as well as impurity elements - oxygen, sulfur, etc. by using balance (total) reaction. Efficiency of refining processes at out-of-furnace treatment of iron-carbon melts depends on a structurally-chemical condition of ladle slag. These slags are formed from the liquid furnace slags that enter the ladle when metal tapping from a melting unit and in the process of adding reduction alloys, ferroalloys, solid slag-forming mixtures consisting of precalcined lime, calcium fluoride and other materials which increase the total mass of slag as a result of chemical reactions with impurity elements of molten metal.

Results and Discussion

The amount of slag that enters the ladle at metal tapping from converter depends on the method and slag cut-off device construction in the beginning and end of tapping. For example, the regulatory documents regulate amount of converter slag in the ladle not more than 5.5 kg/t without taking into account ladle slag appeared after addition of ferroalloys and solid slag mixtures at the enterprises of corporation "Siemens – YAI".

Coating slag in the ladle is referred to three-component system SaO-Al_2O_3-SiO_2 which includes three-chemical compounds - anorthite and gehienite - the basic minerals of metallurgical slags as well as eutectics which makeup is unspecified [3]. The eutectics is a chemical compound existing only in the liquid state [4] in a wide area of homogeneity. This eutectics is decomposed during crystallization on the initial components forming solid solutions with periodic structure. Eutectics as intermediate phase between initial components differs by the lowest melting temperature and maximum structural disorder at minimum overheating over melting point.

The structural disorder appears as a result of thermal or chemical effect. In the first case, polymeric structure of slag [5] consisting of centrally symmetric ionic complexes of elements (Al^{3+}, Si^{4+}) and end cations of calcium (Ca^{2+}) with oxygen ion (O^{2-}) is decomposed at certain overheat temperatures depending on the strength of chemical bonds. First, bonds calcium - oxygen break with the formation of free ions Ca^{2+} and O^{2-} when the slag system passes into activated condition [6]. The reactive capacity of such slag depends on density of oxygen ions because its bond with calcium is recovered at temperature drop. Adsorption capacity of slag in relation to sulfur is revealed at sulfur concentration twice as much as oxygen, which becomes possible at molization of oxygen ions and its removal into atmosphere at evacuation or slag deoxidation by chemically-active elements with reactive capacity equal or more than calcium. Such components are polyvalent silicon and aluminum and alkaline, alkaline-earth elements.

The known three-component eutectics of stoichiometric composition $3CaOA1_2O_3SiO_2$ in the system CaO-Al_2O_3-SiO_2 selected as optimum composition of refining slag contains 51 % CaO + 31.0 % $A1_2O_3$ + 18.0 % SiO_2 with basic capacity $B = CaO/SiO_2 = 2.8$; module $M = CaO/SiO_2+Al_2O_3 = 1.04$ and melting temperature ~ 1350 °C [3]. The structural formula of eutectics $Ca_6Al_4Si_2O_{16}$ represents a centrally symmetric polygonal cell in the liquid state (**Figure 1**) with saturated chemical bonds of ionic type that eliminate reactive capacity of slag.

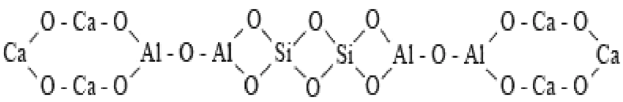

Figure 1. Structural formula of eutectics $Ca_6Al_4Si_2O_{16}$

The reactive capacity of such slag appears in the activated condition due to its deoxidation by chemically-active elements - carbon, silicon, aluminum, etc. They bond end atoms of oxygen in gaseous (CO, CO_2) or oxide phases (SiO_2, $A1_2O_3$) with the formation of free calcium ions and reactive (activated) slag phase capable to adsorb slag and nonmetallic inclusions - products of deoxidation, sulfur removal, etc.

Thus, reaching the maximum extent of structurally-chemical disorder (activated condition) of refining slag at specified temperature of molten metal is a sufficient condition to increase efficiency of steel ladle treatment.

The type of additives (metallic, slag-flux), their makeup and properties define amount and sequence of certain stages of refining mechanism, microalloying and inoculation [7] at all stages of out-of-furnace treatment.

The following industrial grades of ferroalloys are considered as ferroalloys and rich alloys: ferromanganese FMn78 on the basis of solid solution of stoichiometric composition $FeMn_4$, ferrosilicon FS65 on the basis of intermetallic $FeSi_4$, silicocalcium SC25 on the basis of silicide Si_4Ca, synthetic ferroaluminum FA30 on the basis of intermetallic FeAl instead of secondary alloy AB87 and also flux cored wires filled with grained secondary aluminum instead of aluminum rolled wire, calcium and their alloys (silicocalcium, alumocalcium, alumosilicocalcium).

New solid slag mixtures - synthetic slag mixtures on the basis of three-component eutectics of stoichiometric composition $3CaOA1_2O_3SiO_2$ - are prepared from components of solid slag mixtures on the basis of precalcined lime (CaO) and broken fireclay brick containing aluminosilicate $Al_2O_33SiO_2$ as alternative of expensive and scarce calcium fluoride. When hot metal tapping in the ladle, lumpy ferroalloys and solid slag mixtures are added: ferrosilicium and ferroaluminum for slag and metal deoxidation, ferromanganese - for sulfur removal and steel alloying, ferrosilicium is also used for alloying. Out-of-furnace treatment of steel includes deoxidation of metal and ferrous furnace slag, sulfur removal and alloying by manganese and silicon, forming refining slag and its activation due to deoxidation by synthetic ferroaluminum, slag assimilation of nonmetallic inclusions - deoxidation and sulfur removal products. In this conjunction, initial stages of steel ladle treatment mechanism are presented by consecutive series of structurally-chemical reactions (equations 1-6).

As obvious, deoxidation reactions of furnace (1) and ladle (5) slags and also deoxidation and sulfur removal from metal (2, 4), formation of nonmetallic inclusions (1-5) and preliminary alloying (5) take place at the first (initial) stage of steel ladle treatment.

At the second stage of ladle treatment, refining slag is formed with target adsorption capacity to nonmetallic inclusions for assimilation and dissolution of silica $(12SiO_2)_s$, aluminum oxide $(13A1_2O_3)_s$ and manganese sulfides $(2MnS)_s$. It is necessary to activate coating slag due to ferroaluminum deoxidation and obtain deficiency of concentrations of basic and acid components from stoichiometric composition in the field of homogeneity of three-component eutectics. Refining mechanism at the second stage when hot metal tapping is represented by a series of structurally-chemical reactions (equations 7-10).

At this stage, refining slag is formed from precalcined lime and broken fireclay brick (equation 7) and activated (equation 8), metal is deoxidated additionally and aluminum oxides (equations 8-9) are dissolved in the oxide-sulfide coating slag (equation 10). As a result of summing up reactions 6 and 10, the balance reaction of refining mechanism when metal tapping in the ladle is expressed as equation 11.

Consumption indexes of additives for deoxidation of furnace and ladle slag, deoxidation and sulfur removal of metal, silicon and manganese alloying and also amount and chemical composition of coating slag are defined from equation 11. Powdered compact materials (PCM) in the form of flux cored wires are added in the ladle metallurgy facilities (LMF) for final deoxidation and steel sulfur removal. Mixture of silicocalcium SC25, secondary aluminum granules and technical calcium is prepared as filler. It contains 37.3 % Si +26.7 % Ca + 36.0 % A1 and corresponds to stoichiometric composition of $Si_4Ca_2Al_4$. Steel ladle treatment mechanism at the LMF stage is presented by chemical reactions 11-14.

$$3(FeO)_s+2(FeAl)_s \rightarrow (Al_2O_3)_s + 5\,Fe_{Me} \quad \text{(Eq. 1)}$$

$$3(FeSi_4)_{Me}+24[O]_{Me} \rightarrow 12(SiO_2)_s + 3Fe_{Me} \quad \text{(Eq. 2)}$$

$$22(FeAl)_{Me}+33[O]_{Me} \rightarrow 11(Al_2O_3)_s + 22Fe_{Me} \quad \text{(Eq. 3)}$$

$$(FeMn_4)_{Me}+2[O]_{Me}+2[S]_{Me} \rightarrow 2(MnO)_s + 2(MnS)_{Me} + Fe_{Me} \quad \text{(Eq. 4)}$$

$$2(MnO)_{Me} +2(FeAl)_s+ [O]_{Me} \rightarrow (Al_2O_3)_s + 2Fe_{Me}+ 2[Mn]_{Me} \quad \text{(Eq. 5)}$$

$$\sum: 3(FeO)_s +60[O]_{Me}+ 2\,[S]_{Me} +3(FeSi_4)_{Me} +4(FeAl)_s +22(FeAl)_{Me} +(FeMn_4)_{Me} \rightarrow$$
$$\rightarrow 33Fe_{Me} + 2[Mn]_{Me} +12(SiO_2)_s+13\,(Al_2O_3)_s + 2(MnS)_s \quad \text{(Eq. 6)}$$

$$40(CaO)_s+ (Al_2O_33SiO_2)_s \rightarrow (40CaOAl_2O_33SiO_2)_s \quad \text{(Eq. 7)}$$

$$(40CaOAl_2O_33SiO_2)_s+2(FeAl)_s+[O]_{Me} \rightarrow (Al_2O_3)_s+ 2Fe_{Me}+(Al_2O_33SiO_238CaO2Ca^+)_s \quad \text{(Eq. 8)}$$

$$(Al_2O_33SiO_238CaO2Ca^+)_s +2[S]_{Me} + (Al_2O_3)_s \rightarrow (2Al_2O_33SiO_238CaO2CaS)_s \quad \text{(Eq. 9)}$$

$$\sum: 40(CaO)_s+(Al_2O_33SiO_2)_s+2(FeAl)_s+[O]_{Me}+2[S]_{Me} \rightarrow$$
$$\rightarrow 2Fe_{Me} + (2Al_2O_33SiO_238CaO2CaS)_s \quad \text{(Eq. 10)}$$

$$3(FeO)_s+40(CaO)_s+(Al_2O_33SiO_2)_s+61\,[O]_{Me}+4[S]_{Me}+3(FeSi_4)_{Me} + 6(FeAl)_s+$$
$$+22(FeAl)_{Me}+(FeMn_4)_{Me} \rightarrow 35Fe_{Me}+ 2[Mn]_{Me}+(15Al_2O_315SiO_238CaO2CaS2MnS)_s \quad \text{(Eq. 11)}$$

$$4(Si_4Ca_2Al_4)_{PCM} \rightarrow 4\,(Si_4Ca_2Al_4)_{Me} \quad \text{(Eq. 12)}$$

$$4(Si_4Ca_2Al_4)_{Me} + 9[O]_{Me}+ 4[S]_{Me} \rightarrow (Al_2O_3)_s+(SiO_2)_s+4(CaO)_s+4(CaS)_s+$$
$$+15[Si]_{Me}+14[Al]_{Me} \quad \text{(Eq. 13)}$$

$$\sum: 4(Si_4Ca_2Al_4)_{PCM} + 9[O]_{Me}+4[S]_{Me} \rightarrow 15[Si]_{Me}+14[Al]_{Me}+ (Al_2O_3)_s+ (SiO_2)_s+ 4(CaO)_s+ 4(CaSi)_s \quad \text{(Eq. 14)}$$

Balance reaction of ladle treatment mechanism as a result of summing up reactions (11) and (14) looks as equation 15. Reaction 15 (*s* - slag, *Me* – metal, *PCM* - powdered compact materials) outlines the mechanism of deoxidation, sulfur removal, alloying and inoculation of nonmetallic inclusions at steel ladle treatment when metal tapping from a melting unit and on the LMF.

Resource-saving technology of converter steel out-of-furnace treatment was suggested on the basis of above-mentioned mechanism of refining processes of iron-carbon melts. It includes a consecutive series of operations in the ladle when metal tapping and on the LMF.

Converter melt is an intermediate product for steelmaking and characterized by raised oxidation of metal - (0.08-0.12) % $[O]_{Me}$ and slag - to 20.0 % FeO at sulfur content 0.020-0.030 %. As mentioned earlier, such filler materials as ferrosilicium FS65, ferromanganese FMn78, ferroaluminum FA3O are used when hot metal tapping in the ladle.

Industrial grades FS65 and FMn78 are standardized materials whereas FA30 is a synthetic alloy developed by authors of present paper for converter steel deoxidation [8-10]. Its density is 2.0-2.5 times higher than density of alloys AB87, therefore they are applied for metal and slag deoxidation and not oxidated by atmosphere oxygen as alloy AB87 which density is less than density of ladle slag.

At the first stage of ladle treatment, preliminary deoxidation and sulfur removal from metal with the formation of nonmetallic inclusions are carried out, and activated refining slag is built up.

The balance equation of chemical reaction (15) allows defining consumption indexes of filler materials in steel ladle under converter as well as amount and chemical composition of coating slag.

Appeared free-running oxysulfide slag in amount 4.9 kg/t contains 18.5 % SiO_2 +31.4 % Al_2O_3 + 43.6 % CaO + 3.0 % CaS + 3.5 % MnS with basicity 2.4; with slag module ~ 1.0 and corresponds to homogeneity area of three-component eutectics of stoichiometric composition $3CaOAl_2O_3SiO_2$ and adsorbs 2.6 % S + 14.8 % SiO_2 + 29.2 % Al_2O_3 at removal of 0.216 kg/t - FeO; 0.976 kg/t - $[O]_{Me}$ and 0.128 kg/t - $[S]_{Me}$.

The sequence of technological operations on addition of filler materials for ladle treatment of converter intermediate product is as follows: FA30 (2.32 kg/t) → FS65 (0.5 kg/t) → FMn78 (0.28 kg/t) → synthetic slag mixtures (2.5 kg/t), where FA30 is used for metal and slag deoxidation, FS65 - for metal deoxidation, FMn78 - for sulfur removal and metal alloying, synthetic slag mixtures - for assimilation and removal of nonmetallic inclusions.

We assumed that the final refining slag in the steel ladle in amount 5.5 kg/t contains (mass. %): 17.3 SiO_2 + 29.4 Al_2O_3 + 42.4 CaO + 7.8 CaS + 3.1 MnS at basicity 2.45 and module of slag 1.1. Adsorption capacity of such slag is (mass. %): silica – 14.1; aluminum oxide – 27.6; lime carbonate – 2.0; sulfides – 10.9 (4.6 - on sulfur).

Extent of steel desulfuration was defined by sulfur decrease in samples of metal 2-1 and 2-2 on LMF, the total extent of desulfuration - on metal samples on turndown (0.030 %) and 2-2 (0.004 %) was 86.7 %.

The adsorption capacity of refining slag was evaluated by the specified chemical composition of synthetic slag mixtures and the final ladle slag at set mass 2.5 kg/t and 5.5 kg/t respectively. Additional content of CaO is considered after addition of ПКМ-А35С35К25 powdered compact material on the LMF.

Process variables of metal refining in the steel ladle are presented in **Table 1**.

Technological efficiency of obtained results is considerably higher as compared to the known data [11] about sulfur removal from converter steel treated by solid slag mixtures (CaO: CaF_2 = 4:1) in amount 4.0-6.0 kg/t and silicocalcium of grade SC30 in amount 1.5-2.0 kg/t. Extent and depth of desulfuration on the LMF is 3-4 times lower, namely: 20.5 against 76.5 % and 0.012 against 0.004 % respectively.

Low efficiency of ladle treatment is caused by high basicity of refining slag (5.1 against 2.45) which decreases adsorption capacity (mass. %) in relation to sulfur in slag (0.39-0.43 against 2.5) and to aluminosilicate - (23.8 Al_2O_3 and 12.0 SiO_2 against 29.4 and 17.3).

Resource saving technology of converter steel deoxidation in the ladle depending on grade

$$3(FeO)_s+40(CaO)_s+(Al_2O_33SiO_2)_s+70[0]_{Me}+8[S]_{Me}+3(FeSi_4)_{Me}+6(FeAl)_s+22(FeAl)_{Me}+$$
$$+FeMn_4)_{Me}+4(Si_4Ca_2Al_4)_{PCM} \rightarrow 35Fe_{liquid}+2[Mn]_{Me}+15[Si]_{Me}+14[Al]_{Me}$$
$$+(16Al_2O_316SiO_242CaO6CaS2MnS)_s \qquad \text{(Eq. 15)}$$

Table 1. Process variables of steel refining

Sample number on LMF		2-1	2-2
Sulfur content, mass. %	Metal	0.015-0.020	0.003-0.005
		0.017	0.004
	Slag	2.0-3.0	4.0-5.0
		2.5	4.5
Adsorption capacity of slag, mass. %	CaO	-	2.0
	SiO_2	14.8	17.3
	Al_2O_3	29.2	29.4
	CaS	3.0	7.8
	MnS	3.5	3.1
Sulfur distribution factor		147.0	1125.0
Extent of desulfuration, mass. %		76.5	
Basicity of slag		2.40	2.45
Module of slag		1.0	1.1

* minimum and maximum values are in numerator, and average - in denominator.

makeup of steel as well as composition and quality of filler materials was suggested in publications [9,12]. In particular, new solid slag mixtures and modifying agents developed by authors of the present paper were not applied in references.

The economic benefit of recommended technology can be received at several stages of ladle treatment:

- Increase of molten metal yield due to iron of filler materials in amount 2.0 kg/t which is not considered in factory practice;

- Substitution of imported calcium fluoride in commercial solid slag mixtures on broken fireclay brick when slag cost becomes equal to factory price of precalcined lime at reduction of specific consumption of solid slag mixtures in 2 times (2.0-2.5 kg/t against 4.0-4.5 kg/t);

- Substitution of pig aluminum AB-87 in equal amounts (2.0-2.5 kg/t) on ferroaluminum FA30 which cost is 30 % less;

- Substitution of aluminum rolled wire in equal amounts (0.3-0.5 kg/t) on aluminum in granules, which is a part of complex filler of powdered compact materials and which cost is 30 % less.

Conclusions

1. The method of stochastic analysis of iron-carbon melts refining mechanism by added metal and slag-flux materials with the use of secondary materials was developed.

2. The mechanism of slag formation and converter steel refining in the ladle when steel tapping and metal shaping-up was investigated, consumption indexes of additional materials at ladle steel treatment and also amount, composition and adsorption capacity of refining slag were determined.

3. The flow diagram of resource-saving technology of converter steel ladle treatment that regulates the sequence of operations related to addition of set amount and composition of additional materials: ferroaluminum FA30 (2.3kg/t) → ferrosilicium FS65 (0.5kg/t) → α ferromanganese FMn78 (0.3kg/t) → synthetic slag mixtures (2.5kg/t) → flux cored wire with alumosilicocalcium C35K25A35 (0.25kg/t) at filling of steel ladle up to 3/4 of its height. This technology ensures removal of oxygen 0.98 kg/t and sulfur 0.13 kg/t at extent of desulfuration more than 70 %.

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* Published in Russian

Received February 02, 2010

Анализ рафинировочных процессов ковшевой обработки стали

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В статье предложена ресурсосберегающая технология ковшевой обработки стали металлическими и шлако-флюсовыми присадочными материалами с использованием порошковых проволок, синтетических сплавов и шлаков из вторичного сырья, позволяющая в 1,5-2,0 повысить технологическую эффективность внепечной обработки стали.