Features of slag-metal interaction at electroslag remelting of heavy ingot

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Abstract: The new look on the ESR process allows us to formulate physic-chemical model of process based on equilibrium thermodynamic principles. Using this model we have compared the refining ability and oxidizing action of fluoride and two oxide-fluoride slags in argon atmosphere and in the air. It has been indicated that even if the protective atmosphere is used, slags are still able to oxidize the metal, and the extent of desulphuration is determined by the content of CaO in the slag.

Key words: electroslag remelting, heavy ingot, slag-metal ratio, equilibrium composition, slag-metal-gas interaction.

1. Introduction

Electroslag remelting process (ESR) is on the stage of renaissance. For the last 5 years a big number of furnaces for large ingots (50-400 tons) has been put into operation. New materials, demands for increasing energy efficiency and ESR metal quality led to the necessity of more precise realization of the nature of interaction in the complex metal-slag- gas system taking into account traditional and new types of ESR (remelting in protective atmosphere and under pressure, in current supplying mold i.e. ESR with liquid metal application , etc).

2. Basic physical-chemical principles and technical features of electroslag remelting process

Traditional electroslag remelting process (figure 1) is thoroughly investigated. Most of well-known principles of complex interactions in metal-slag-gas system are based on the results of direct chemical analysis of phases compound for a certain melt.
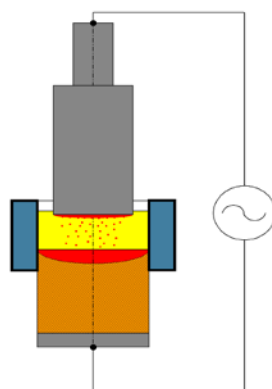

Fig. 1 Traditional electroslag remelting process diagram

Thus, it is generally accepted that during electroslag remelting process the oxygen and sulphur content descends mainly due to nonmetal inclusion removal. A great number of known data can be found in works of B.I. Medovar [1-3] and his followers [4-6]. However, the published data often isn't complete, and, in spite of process being widespread in the world, there are not many works with detailed and systematic study of compositional change of slag, metal and gas.

Moreover, physical-chemical processes within traditional electroslag remelting process in the open air is usually studied in its steady state, considering that in this case the system consists of some constant volume of slag, metal and gas. In fact, liquid metal appears in the end of the electrode as a film which the drops come off. While falling the drops go through almost the whole thick slag till getting into metal bath. The metal bath constantly solidifies forming an ingot, and its depth usually doesn't exceed the ingot radius. So, liquid metal leaves the interaction zone in relatively short time. In other words, the reactive system metal-slag changes all the time due to again remelting part of the electrode.

The reactions completeness is achieved by the developed surface of drop-film mass transfer and also by constant contact of surfaces of slag and metal baths. Active reaction takes place due to great overheat of metal and slag (higher than melting point). The overheat makes 50-200 degrees for a metal (sometimes more) and 100-300 degrees for a slag.

That's why the fact that the proportion of metal and slag in electroslag process at every certain moment is maximum close to equilibrium state allows us to use the principles of equilibrium thermodynamics.

While creating the model of the process such things were taken into account – the fact that the ESR is an open system where momentary composition may be considered equilibrium, and the mass of interacting phases changes in different periods of time.

The starting quantity of slag is determined by the remelting process parameters, as physical features and height (volume) of slag layer determine the amount of heat generated in the process. So, the correlation of reacted phases of system in the beginning of process and in the steady phase of remelting differs, because at the beginning the whole amount of slag reacts with the small amount of metal which grows to the mass of the ingot.

What is more, there are two variants of organizing the process. The first one involves the feeding of the major amount of slag (more than 85-95%) in the beginning of the process and adding new slag (0.1 -1% of initial mass) in equal periods of time (usually 15-60 min) during the process. The second variant involves single slag feeding of the whole amount of slag in the start of remelting.

The first variant is widely used when the length of an ingot is significantly bigger than its diameter (usually in small-section ingot remelting). In this case the loss of slag skull should be compensated so that the process stays stable as the heating capacity of slag bath depends on its volume. Thus, the slag and metal phases renovate (relatively and constantly).

The second variant is made use for forging and slab ingots, in which the correlation of length and diameter hardly ever goes beyond 3. In spite of small length, large ingot remelting takes quite long time (50 hours and more), because of low speed of their withdrawing (determined by the speed of consolidation).

All these features mentioned above appear to be very important in large ingot remelting when it is necessary to take care of composition stability from any height of ingot.

As a rule, the steels used in the process have complex composition and include many alloy elements, also easily oxidable ones. The minimal concentration of sulfur, oxygen and hydrogen must be provided as the quality demands to heavy ingots have increased lately.

Due to that fact, we have made an attempt to make a physical-chemical model of large ingot remelting in protective atmosphere of neutral gas. Moreover, the numerical calculations of the traditional process were made in order to justify the limits of oxygen content in the atmosphere of mold and prevent the oxygen content pick up in the metal.

The large forging ingot from steel grade 316L mass 100 t, diameter 2000 mm, length 4057 mm was taken as a model. The speed of remelting was taken 2000 kg/h. The specific slag consumption was 25 kg/t of metal. The initial mass of slag makes 2500kg, height of slag layer - 306 mm. The temperature of the process was 1700 degrees. Duration of remelting - 50h.

3. Physical-chemical model of heavy ingot remelting in protective atmosphere

ESR process in neutral atmosphere may be presented differently in comparison with traditional process with reacting gas. As the gas phase doesn't include component interacting with metal or slag, it (the gas phase) by its nature is the accumulator of "fumes" of interacting phases: slag-metal. Defining the system composition we have supposed that during the process the volume of argon is growing steadily. The growth equals average quantity of argon mass flow in secondary metallurgy processes (1-10 m^3/h). In this case two phases of system can be regarded "in dynamics" of the process: all metal of the electrode goes through the slag layer interacting. As a consequence, the mass of system is growing steadily due to metal accumulation.

We will emphasis again that developed interacting surface the equilibrium state is considered to be achieved even before the moment the metal gets into the metal bath; no flow of matter from the gas phase (no air).

Thus, at every moment the reacting system consists of total amount of slag (the loss by slag skull is considered small and/or compensated) and mass of electrode having been remelted by that moment.

Slag - metal (remelted part of consumable electrode) mass ratio is instant slag consumption at the moment (figure 2), difference in slag skull of the ingot is taken into account.
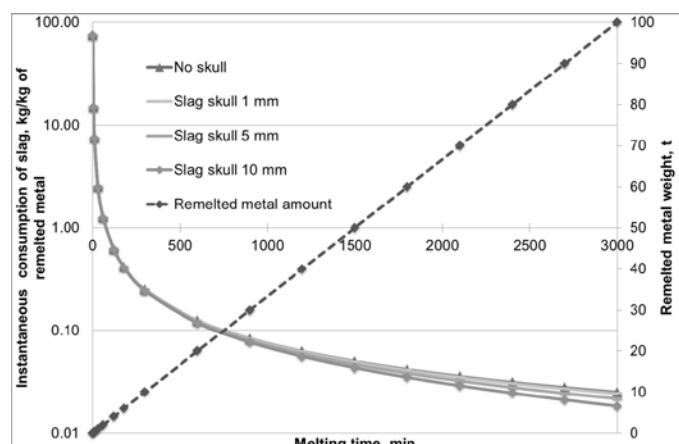
Figure 2 Time-prognosis of changing of ingot mass and instant slag consumption in ESR of the large forging ingot, diameter 2000 mm, mass 100 t. Hereinafter a full line belongs to trends were plotted by main vertical axis as well as a dashed line – by additional vertical axis.

It is shown that slag-metal mass ratio at first minutes of remelting is 75 kg/kg, and goes down sharply during 2 hours, and noticeably - during next 15 hours.

The amount if the loss by slag skull, naturally, depends on its thickness (figure 3) and isn't more than 10% during the first third of remelting, and the amount of loss for slag skull is less than 1mm and doesn't go beyond 3% during the whole remelting.
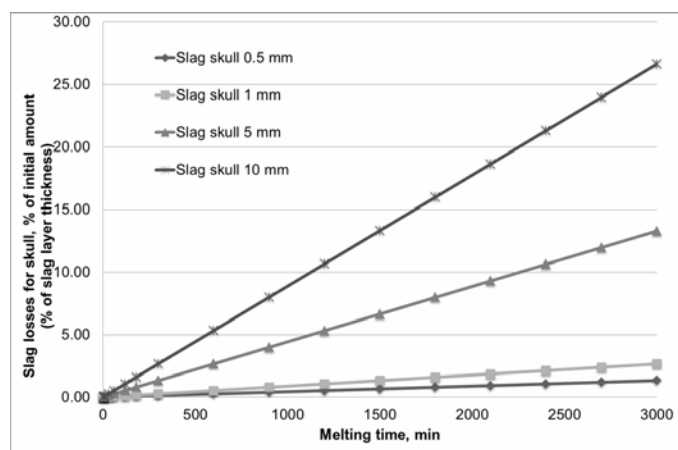

Figure 3 The loss of mass of slag (height of slag layer) by slag skull of different thickness during the ESR of the large forging ingot, diameter 2000 mm, length 4057mm.

This is how the height of the slag in mold decreases in the process of forming a slag skull. Maximum decrease of height is 4.06; 8.12; 40.67 и 81.54 mm for 0.5; 1; 5 и 10 mm of slag skull, correspondingly.

It is obvious that if the slag skull doesn't go beyond 5mm, there is no need to use new (additional) slag for compensating its height. It is not necessary to feed new slag in the process of remelting.

On the other hand, the composition of slag can change in the process of remelting, so it should be corrected by the

means of feedings of different components on order to save the initial slag composition.

To justify the necessity of slag composition correction we need to examine and analyze it in the process of remelting. The physical-chemical calculations of equilibrium in system slag-metal-gas have been performed for the common phases of ingot under examination - steel 316L and three compositions of slag (fluoride and two oxide-fluoride). The compositions of examined phases are shown in the tables 1 and 2.

Table 1. Composition of steel 316L

Steel mark	Elements content (mass%)										
	Fe	C	Si	Mn	P	S	Ni	Cr	Mo	N	Al
Steel 316LN	60.97-69.02	≤ 0.035	≤ 0.75	≤ 2.00	0.01	0.01	10.0-15.0	16.0-18.0	2.0-3.0	0.1-0.16	≤ 0.08

Table 2. Composition of slags

№	Analyzed compositons (mass%)				
	CaF2	Al2O3	CaO	SiO2	MgO
1	30.0 ± 3.0	32.0 ± 3.0	33.0 ± 3.0	≤ 0.6	3.5 ± 1.5
2	58.5 - 62.5	22.5 - 31.5	10.0 - 15.0	-	-
3	≥ 97	≤ 1.5	≤ 2	≤ 0.5	-

The calculations show that all slags have oxidize effect on metal even in the protective argon atmosphere (figure 4).
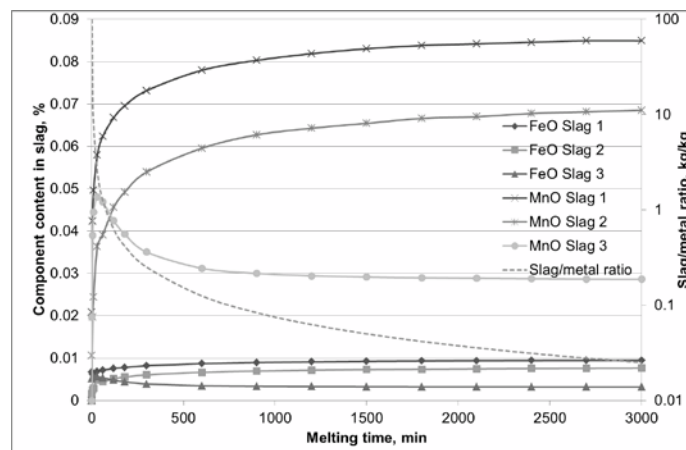

Figure 4 Calculated content of ferrous and manganese oxides in slags in the process of ESR of the 100t 316 steel ingot.

The ferrous and manganese oxides appear in all slags at the beginning of the process. In the process of remelting with only fluoride slag the content of ferrous and manganese oxides decreases, but their content increases steadily in the systems with oxide-fluoride slags. It means that even in protective atmosphere slags have oxidizing effects on the produced metal. In steel there are elements more active (according to oxygen affinity) than manganese and ferrum – calcium, aluminum, titanium, silicon. Their oxidizing is more intensive. Figure 5 shows the compositional change of components in the examined slags in the process of remelting.

It is shown also that examined slags can remove sulfur from the metal in CaS. The run of the curve of compositional change of CaS is identical to all other slags, and the amount of CaS produced till the end of the process equals 0.6-0.8% of slag mass and is determined mostly by the CaO content in a slag.
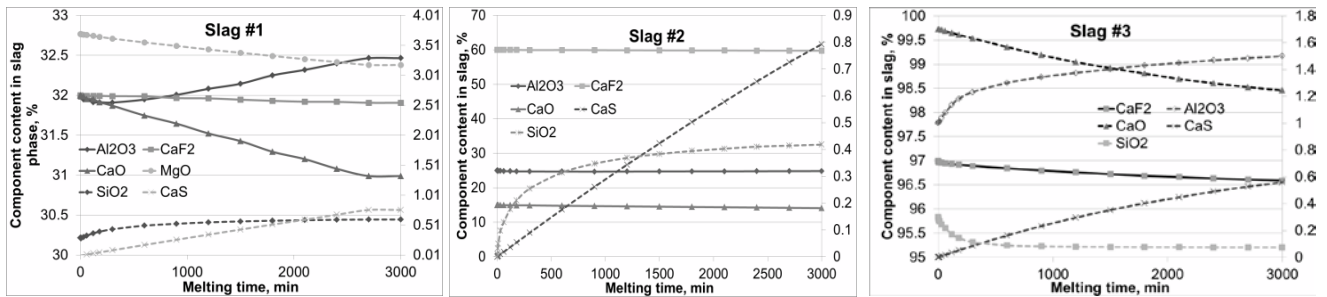
Fig. 5 Change of components content in slag phase in different time periods (different slag-metal ratio in the system) for the examined ingot.

In any case, even despite the neutral atmosphere the content of aluminum oxide in slag increases. The aluminum (from steel compound) oxidizes and the oxide transforms into slag. It should be noted that the aluminum content also grows into gas phase in the form of volatile fluoride Al_{F3}.

The reaction of silicium in oxidize slags is similar to that of aluminum. In the pure fluoride slag (where oxygen amount is much less) silicium oxide forming by oxidizing of silicium from steel is limited, and its content in slag decreases (within its weak concentration) because of forming of silicium fluoride SiF_4.

The rated content of volatile fluoride in the gas phase increases in the process of remelting due to the initial content of fluorspar in slag, although being insignificant for all three slags. The overall loss of fluorspar in fluorine fumes and formed fluorides doesn't go beyond 0.5%.

The components behavior in metal phase stays within the traditional conceptions, and their compositional changes are minor and correlate with that in the slag phase. Therefore we didn't show these pictures in this paper.

Thus, on the basis of physical-chemical modeling of ESR process of large ingot in the neutral atmosphere it is shown that all slags have oxidizing effect on metal. The higher the content of oxides (Al_2O_3 and SiO_2) is, the stronger the effect. The desulfurization takes place, and its extent depends on the basicity of slag.

4. Physical-chemical model of ESR process in open air

Unfortunately, it is not possible to narrow down the system in the air to two reactive phases. The air includes oxygen, nitrogen, and hydrogen, that merge in slag and metal and interact with their components producing oxides, nitrides and less hydride in solidified ingots. In case when the gas phase effect cannot be neglected the suggested model is incorrect and the process cannot be studied in dynamics, although the slag-metal ratio changes in the same way as in the previous model. The solubility of gases in solid metal is much less than in the liquid one. Hence, only liquid metal bath should be considered in system formation.

Moreover, in order to create the correct amount of air in the system we should know the diffusivity coefficients and flowing of oxygen and other components of gas phase into slag and metal, and products of interaction in opposite direction during a process. So, though in the previous model the dynamics of process could be evaluated altogether, for

the ESR in the open air we can only make a model of the steady phase.

Setting the goals of modelling it was assumed that the interacting system consists of a slag phase with mass 2500 kg (total volume) and a metal phase with mass 14t which corresponds the maximum mass of liquid bath (a sphere with the same diameter as the one of the ingot), and a gas phase - air (21% of oxygen).

As the gas phase doesn't interacts with liquid metal directly, the oxidizing effect of it on the metal is a complex process consisting of such stages as – oxidizing of (FeO) to (Fe$_2$O$_3$) on the surface of "gas phase-slag" boundary, transfer of produced (Fe$_2$O$_3$) in the layer of slag to the "slag-metal" border, and interaction of (Fe$_2$O$_3$) with liquid metal on this border. Each of these stages includes diffusive and kinetic stages, where the diffusion (transfer of substance) is the limiting one.

Calculation of equilibrium content of oxygen in the system with the temperature of 1700°C using the thermodynamic data [7] showed that partial pressure of oxygen in the gas phase, equilibrium with oxygen activity in metal – 10 ppm (for steels deoxidized by aluminum) makes $3.12 \cdot 10^{-8}$ Pa ($3.12 \cdot 10^{-13}$ at). All things considered, the minimal amount of air in which the additional oxidizing of active elements of the metal doesn't occur is 10^{-13} at. The content of oxygen in the steel is 0.0114%, the activity ratio of oxygen is 0.0878; of ferrous oxide in steel - 0.0878, in slag - 0.0029.

From the point of view of manufacturing technology, these results are important. The fact that the content of oxygen in industrial argon is usually $5\text{-}7 \cdot 10^{-6}$ at (i. e. the volume of oxygen isn't more 0.0007%) should be taken into consideration and be dealt with (e.g. by additional purification of argon) while remelting the steels with active elements (Al, Ti). If we use the received data of the equilibrium content of ferrous oxide in slag (FeO) in slag 0.05-0.08% (1.25-2 kg), we can rate the growth of oxygen content in the metal. The calculations show that such mass of (FeO) is able to transmit and transfer 0.139-0.222 kg of oxygen to the metal, and that will lead to the increase of the amount of oxygen in steel by 10-16 ppm.

The data received is proved by the remelting process practice, which provides for slag deoxidizing by adding active elements (usually aluminum) in order to produce solid, dense ingot and avoid alloying element losses from steel. Defining and calculation of actual quantity of elements in metal, slag, and gas phase coefficients requires great research work we are started to do.

5. Conclusion

Main principles of physic-chemical model for ESR process in protective atmosphere and on open air were formulated. The ratio of slag and metal changes while melting from very big values to usual rated consumption: e.g. for 100t ingot – from more than 75 kg per kg of metal to 25 kg per ton of metal.

For neutral atmosphere case it is possible to designate gas phase volume in reacting system that allows us to make prediction of system equilibrium compounds in dynamic. The oxidizing action of fluoride and two oxide-fluoride slags was shown: even in protective atmosphere slags have oxidize effect on the produced metal. The desulfurization takes place, and its extent depends on the basicity of slag. The volatile fluorides content in gas phase doesn't go beyond 0.5%.

The system in the air it is not possible to narrow down to two reactive phases because gas phase effect cannot be neglected that's why for the ESR in the open air we can only make a model of the steady phase. It was found that the minimal amount of air in which the additional oxidizing of active elements of the metal doesn't occur is (10^{-13} at) that is less than the content of oxygen in industrial argon. It was shown that 0.05-0.08% of (FeO) in slag is able to transfer 0.139-0.222 kg of oxygen to the metal, and that will lead to the increase of the amount of oxygen in steel by 10-16 ppm.

Studying of the mechanism and thermodynamics of processes in system metal-slag-gas allows to compare refining ability and oxidizing action of slags, as well as to predict their behaviour at durable melt and to define optimum variants of the electroslag process organization of at melting of heavy steel ingots.

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