SLAG IN THE PROCESS OF ESR: EXECUTIVE PART AND URGENT TASKS

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Abstract: Solving the new tasks of increasing the purity and quality of the ESR ingots the creation of effective slag composition has been initiated. The demands to the slag and urgent tasks of its improving were formulated. There were given some results of the experimental research on the development of spontaneously disintegrating slag to melt long hollow ingots.

Keywords: slag, electroslag process, chemistry, physical properties, hollow ingot.

1. Introduction

The metal of electroslag remelting (ESR) is widely used nowadays to produce critical and especially large items for petrochemical industry, atomic energetic, and metallurgy. It should be reminded that the process of electroslag remelting was invented in the E.O. Paton Electric Welding Institute and this year we shall celebrate 60 years since the first laboratory ESR ingot was melted [1,2].

On its way to the anniversary the process had several periods. At the very beginning it was a rapid period of development and broadening the sphere of usage around the world, inspired by the armaments race demanding more metal of especially high quality and reliability. The first industrial production was organized by the Soviet Union (in six years after the invention of the process – in 1958) and China (1959). Mostly thanks to the home license and equipment the intense spreading of ESR began in the mid-1960s. Already in 1980s ESR was a well studied standard metallurgic process of producing the high quality complex alloyed steel and ingots. But the decrease of the military orders at the end of the cold war and success of the ladle metallurgy in metal refining led to the period of stagnation in the ESR development. A wide implementation of vacuum degassing provided the reduction of the hydrogen, oxygen and nitrogen (to the smaller extent) content. High level of desulfurization during the ladle metallurgy cycle provided a thousandth of percentage of the sulfur content in metal, annihilating the advantage of ESR on this criterion.

Still the development of ESR did not stop there. In order to respond to the new demands of the gas content in 1980-1990 the ALD company developed ESR in the closed chamber – under pressure (PESR), also in the isolated atmosphere (IESR) and vacuum (VAC-ESR) [3,4].

The process was further improved in 1990-2000 and as the result two completely new modifications appeared: ESR LM (electroslag remelting with the usage of liquid metal) [6,7] and ESRR®[9] (electroslag rapid remelting) aimed at increasing the competitiveness of the process by improving its technical possibilities, cutting down the cost value, increasing the productivity. Big opportunities in production of heavy tonnage ESR ingots are being opened due to the implementing of electroslag remelting process with the usage of short current supplying mold and liquid metal (ESS/ESR MM) which allows to refuse from the production of consumable electrodes and, thus, make the ESR metal cheaper and better [7].

At the same time, due to success of secondary metallurgy there came an understanding of the fact that small productivity of melting and low speed of forming an ingot provides a high density of metal, restricts the development of liquation processes, and guaranties a high yield of metal.

That is why today we observe a new expansion of electroslag remelting. The furnaces are being built around the world to produce the ingots from the high quality and high-alloyed steel and alloys and for heavy forging. Lets analyze which technical features of the process give the undeniable advantages and what are the restriction of the process today and possibilities of their overcoming.

2. The role of slag in ESR, main technological possibilities and restrictions of the process

Judging by the title it is clear that the key component of electroslag process is slag. The history of slag for ESR began with the fluorine slag on the basis of the fluorspar, the main component of which is calcium fluoride [8]. CaF_2 makes a melt having good electro conductivity (mostly ionic type) and sufficient resistance, excellent fluidity, does not create non-stable modifications under temperatures of the process and does not oxidize the metal. But it is expensive, deficient and ecologically harmful.

The most widespread are the slags of the CaF_2-CaO-Al_2O_3 system in different ratio of their elements with the addition of SiO_2, MgO and others [9]. The diversity of the contents is quite big, as each manufacturer introduces their own contents which slightly vary, but have different marking. The properties of oxygen fluoride slag, naturally, depend on its content. To the common differentiating features belong a wider interval of solidification and a higher oxidizing in comparison to the slag from fluorspar.

In the recent book of the authors [10] there was collected and analyzed a number of experimental and theoretical researches of physical and chemical features of calcium fluoride, and also binary, ternary and multicomponent oxide-fluoride systems on its basis allowing to define viscosity, conductivity, the coefficient of diffusion, density and surface tension of slag implemented in the processes of ESR. But together with the questions evoking a common opinion there is also a divergence in the published numbers of measured properties and analysis of the given results and dependability.

In connection to this below there are summarized the characteristic features of the ESR process and the functions performed by the slag, providing the advantages and restrictions of the process and quality figures of the melted ingots.

Thus, in the slag layer a heat is produced which is necessary for the melting of consumable electrode. A slag bath providing the constant, long and regulated heat supply allows to control the forming of the ingot (especially in the new modifications of ESR process), which provides the balanced structure of the ingot, the absence of shrinkage and axial defects, the reduction of zone of liquation. A high metallurgic quality of the ingot during the ESR increases the metal yield in a third and more in comparison to the big ingots of the open air melting and casting. The characteristic feature of the ESR metal is the equal spreading of all phase components over the cut of the ingot which provides an increase of the plastic properties and impact toughness. This is very clearly seen in the metals of heavy plate in z-direction.

The melting and forming of the ingot is done in the copper water-cooled mold without a refractory lining which excludes metal polluting with products of its destruction.

While conducting the current through the slag it is partly straightened, that can cause the process of electrolyze, including the participation of the copper wall of the mold. Such processes are mainly developed in the new construction of current supplying copper mold that can be partially overcome by using slags of mostly ionic conductivity.

Electroslag process can be conducted under the pressure equal to atmospheric, be more or less than it. The most widespread for the melting of complex and critical steel is the variant of ESP under the normal pressure but in the protective atmosphere (argon) which allows to reduce the content of harmful gases in the metal ingot.

The metal temperature is on the level of 1600-1700 C. The melting temperature of the slag is usually lower as it is necessary that the viscosity of slag melt approached the viscosity of metal to exclude the emergence of the suspended particles in a metal and ensuring the active interaction of melts.

The slag is a media that provides the refining, improving and saving the unchanged chemical and phase metal compound. Lets discuss the last thesis in more details. The consumable electrode produces with the implementation of the modern means of ladle metallurgy usually has the given and quite stable content along it. Its melting is executed gradually in drop regime and metal interaction with the slag has a very well developed surface (while melting the end of the electrode, in a liquid drop moving through the slag, on the surface of the boundary metallic bath – slag bath). The reaction completeness is high which allows using the equilibrium thermodynamics in order to estimate the state of the system during the stationary stage.

Irrespective of the content in the process of ESR phosphorus and non-ferrous metals are practically not removed.

If the consumable electrode contains sulphur in hundredth of percent, its concentration in the ingot lowers down in one grade, and if sulphur is contained in one thousandth of percent, its removal may not take place.

The content of oxygen during melting in the open air usually equals not less than to 15-30 ppm. It can be decreased at the expense of diffusive deoxidation through the slag by the active metals (aluminum, calcium[11]) and usage protective atmosphere of argon.

The reducing of the nitrogen content does not take place. Isolation of the melting environment from the contact with the atmosphere may facilitate the saving of the nitrogen content in the electrode. It is possible also to alloy the intended metal by nitrogen from the gas phase as well. Thus the melting should be made in the atmosphere of the nitrogen under the increased pressure. The efficiency is increased by using the arc-slag remelting regime by atomization of the nitrogen molecules in the electric arc [12].

The specific features of the process are such that the usage of the deoxidizing ability of the carbon and conducting the decarbonizing melt need more tricks, and the result is difficult to control.

The content of admixtures in metal of the consumable electrode may be very low. Besides the modern steel and alloys often contain elements that may have high vapour pressure under the temperature of ESP, are able to oxidize and form volatile alloy.

The correction of the metal ingot content by implementing the alloyed admixtures besides their content in the consumable electrode is possible, but undesired, taking into account the complexity of the control over their adoption. Usually it is enough to place admixtures of the oxidizing elements into the slag bath or to use the satellite-electrode from the masteralloy.

The slag forms a layer of skull on the surface of the ingot. The skull prevents the surface from the oxidizing. If the remelting regime had been chosen correctly, the ingot has the surface which allows to roll or forge ingot without any additional cleaning.

The analysis of modern practice of the ESR furnace functioning, the results of theoretical and experimental researches (personal including) of the electroslag process allows to distinguish the requirements to slags, fulfilling of which will allow to enhance the quality of steel ingots and make the modern ESR process more economical.

3. The requirements to the slag of modern ESR processes

Today the slag should provide not only the refining of metal (by the way, one of the names of the process in English speaking literature is “electroslag refining”) by reducing the content of admixtures, but also the preserving the chemical content of metal and preventing the loss of alloying elements, that is, taking into account the modern achievements of secondary metallurgy the requirements to the refining ability at ESR may be significantly lowered.

Thus, the slag should have a sufficient (taken into consideration the purity of a consumable electrode) refining ability for the fullest deletion of sulphur, gases and nonmetal inclusions and serve as a firm barrier for the transferring from the atmosphere into the metal bath of oxygen, nitrogen and hydrogen.

A slag should have:

an optimal electric resistance, providing the sufficient production of the heat in the slag bath;

a low viscosity, slightly increasing with the lowering of temperature, a high interfacial tension on the boundary with metal melt and minimal one on the boundaries with non-metal inclusion;

a stable content that under the condition of significant overheat its liquidus did not change over a lengthy period of melting (dozens and hundreds of hours) or could be easily corrected;

a low original content of hydrogen (it should be provided by the technology of melting in the fluxmelting furnace irrespective of the humidity of original mixture and air, degree of component reduction and carbonization) and the absence of crystallization water and adsorbed humidity.

Formed on the surface of ingot the slag skull should

have a small thickness (1-3 mm), as its increase lowers the heat emission from the ingot and increases the slag consumption;

be dense and have a good metal adhesion to the temperatures of the end of the process of the slow ingot cooling in order to isolate the surface from the oxidizing and forming the oxide during the lengthy contact of the ingot with the atmosphere;

easily peel off after the cooling of the ingot or disintegrate into powder.

All these requirements often contradict each other in practice, and it is quite difficult or almost impossible to create the slag which would meet all of them. Nevertheless in every specific case it is possible to find a slag that would meet the most important requirements.

4. Reasons for Status Quo changing in the assortment of slags for ESR

In our opinion, in order to increase the ESR efficiency and adaptability to manufacture further differentiation of flux metals is needed relating to remelted materials and schemes of remelting.

These are the urgent tasks that are set by the developers of new slag compositions:

1) The quantity of production of the ESR slags remelted in mold with ingot withdrawing has increased recently. It led to the necessity of using “long” slags, which solidify in the wide range of temperatures. The solidification period of the fluoride slag is increased by adding acid oxides. The most common of “long” flux are the ones with silica. However, for the steels with aluminum and titanium such fluxes are useless because of the exchange reactions which results in pick of silicon content in steel up: so the flux properties change a lot due to uncontrolled increase of aluminum and/or titanium oxides in it. New workable fluxes containing such acid oxides as TiO_2, ZrO_2 or other compositions must be developed.

2) Due to wide usage of steels and alloys with alloying elements lowering the temperature of solidus of alloy, and also due to the electroslag technologies using liquid metal a flux with lower temperature interval of remelting (100 – 200°C lower than of the solidus) needs to be developed. Fusible slag (T_m=1150-1300°C) are usually oxide-fluoride eutectic systems with four- or five –component, rarely – salt compositions. Using such slags leads to decrease of specific energy consumption and of heat input in the process, as it allows to decrease superheat of metal over the liquidus temperature. The later is a guarantee of the improvement of the structure of ingot due to faster solidification.

3) Ecological demands and decrease in value of ESR fluxes in cases of preserving their workability causes the necessity to create the fluxes with small content of fluoride and non-fluoride fluxes. Nowadays, a few slags with small content of calcium fluoride exist. However, their melting temperature is too high, and it worsens the transporting properties and leads to big energy consumption. The compositions that would not only remove the fluoride but also solve the task set in item 2 are perspective.

4) It is also vital to develop slags with minimal hydrogen permeability to guarantee with less than 0.5 – 1.0 ppm of hydrogen in remelted ingot without protective chamber, which makes the furnace structure and its operation more difficult.

5) As the hollow ESR ingots manufacture grows it is required to develop ESR fluxes with good removability of slag skull from internal surface of long hollow ingots. The way of solving this problem follows.

5. Case study: self disintegrating slag for hollow ingots manufacture

The extent of the ability to control the solidification process is rather high in ESR hollow ingot production. Intensive heat transfer provides radial-axial crystallization with two opposite fronts of dendrite growth. Small size of the bath and refining effect of slags allow to get the metal without defects common for ordinary ingots casted in usual molds. Hollow ingots have high metallurgic quality and high level of properties of as-cast metal (which often excludes the necessity of deformation) and in deformed metal even in case of small reduction ratio.

As the hollow ingot is formed between two copper water-cooled mold and internal and external surfaces of it are covered with slag skull. Because of big specific surface of hollow ingots slag input for forming slag-skull is bigger. To get thin slag skull we need slag with stable composition and low viscosity. It is important to note that thick slag skull worsens heat-away from ingot to mold. It is especially sensitive in the internal mould, where the tension is much bigger. In order to prevent the leakage inside of the ingot the formed slag skull should be thin and solid. The tension strength of the layer of slag-skull is very important at hollow ingot withdrawing. Multicomponent slags of the system CaF_2-CaO-MgO-Al_2O_3-SiO_2 (ANF-28, ANF-29, ANF-32) meet this demands to the maximum extent.

The ESR process of hollow ingot production is widely used in manufacturing pipes and shells of different mass and width of walls. One of the unsolved problems of production is slag skull removal from the internal surface of ingot. It becomes very hard for pipes with small (narrow) hole [13,14]. If the metal has high adhesion and mechanical strength its removal becomes a problem and requires great labor consumption.

In this regard, attention has been paid to well-known self-disintegrating effect of so called “white slag” used in secondary metallurgy processes. Such a slag has a good ability of refining the metal and assimilation of nonmetal inclusions. It is known that during slow cooling of the “white slag” (the temperature is lower than 525 °C) polymorphic transformation P-2CaOSi0_2 в Y-2CaOSi0_2 takes place and it is accompanied by 10% volume increase. All that leads to cracking and spontaneous pulverizing of slag. Such cracking usually occurs in slags with more than 44-46% of calcium oxide. However, low level of iron and manganese oxides in slags is vitally important.

White slag is well-deoxidized high-basicity refining slag. It should be light grey, yellow, or white. It also should have mat rough surface, freeze on metal section as rusted with thickness 0.5 mm, be fine-pore in fracture, and, during cooling, pulverize in light grey or white powder. It was interesting to investigate actual conditions of white slag production in secondary metallurgy of wheel steel 100 т LF/VD.

The refining slag was directed into ladle on top of the heel of powdered lime (as it is common in secondary metallurgy). The composition of slags selected in the course of experimental remelting of wheel steel with oxidizing the slags on the ladle-furnace is showed in the table 1.

Table 1. Composition of slag in Secondary Metallurgy of wheel steel

heat #	Sampling point	Slag composition						Basicity, units	a_O, ppm	Remarks
		CaO	SiO_2	Al_2O_3	FeO	MnO	S			
1.	LF				3.75	1.10	0.60		24.1	 Black, blistery
	VD	61.6	23.0	6.53	1.30	0.40	0.79	2.68	4.8	 Light, doesn't crumble
2	LF- before input				1.10	0.77	0.66			 Light, blistery, doesn't crumble
	LF - afterInput of 16 kg Al 99% and VD	57.3	26.0	3.98	1.00	0.40	0.77	2.20		 White, crumbles
3	LF - before input			2.79	5.60	3.38	0.14			Black, solid
	LF - input of 40 kg of Al alloy			3.88	3.50	1.46	0.15		25.4	Dark, doesn't crumble
	VD	57.3	26.6	6.42	1.10	0.52	0.46	2.15	3.8	Yellowish, crumbles
4	LF - before input			4.0	2.50	0.73	0.67			Light, doesn't crumble
	LF - input of 60 kg Al alloy			5.75	2.00	0.69	0.72		22.2	 Light, crumbles slightly
	VD	58.0	23.7	7.10	0.80	0.25	0.66	2.45	4.7	 White, crumbles

The consumption of lime was equal to 10-15 kg/t of steel, fluorspar - 1 -5 kg/t of steel. During the comparative melting the slag after the furnace contained a high amount of iron and manganese oxide. After the vacuum degassing of the metal without implementing of deoxidizers the slag became light, but it did not crumble, which proves the incomplete deoxidizing even during the vacuum processing. For more intense deoxidizing of refining slag a powder-like aluminum or its secondary alloy was used. The insertion by the admixtures of the deoxidizers showed that the lowering of slag oxidizing leads to the change of its color – as a result the slag crumbles and has from yellowish to white color. The slag basicity at the end of processing was not more than 2.5 and the consistence of FeO+MnO – not more than 3%.

Depending on the content of metal other oxidizers may be used. During the melting of steel containing a low amount of carbon, aluminum, aluminum-silicon, ferrosilicium are mostly used. For steels with the restricted content of aluminum in the slag there can be used calcium-silicon or ferrocalcium. To oxidize the refining slag during the production of steel grades containing carbon of 0.12 % in the ready metal there may be used coke powder, being injected to the surface over the whole mirror of the slag by portions in 10 - 100 kg depending on the specified content of carbon in melted grade of steel.

All the considerations were the basis for creating a self-disintegrating slag for the ESR process. While composing the slag structure it was considered that conductivity and viscosity are important for slag that may be impossible under a high content of lime as in the ladle slag. That is why it was decided to test the composition with a higher content of calcium fluoride (to increase the conductivity) and a bigger content of aluminum oxide. The analysis of line ESR slag showed that such combinations may be achieved inside the grade interval of ANF-29 slag, the figures of conductivity and viscosity of which are known. Moreover, this slag is quite good for hollow ingots melting.

There was a task to melt a slag with precise chemical composition in order to reach the effect of self-disintegrating. The melting of slag was made in the flux-melting furnace in the graphite crucible from the raw burnt components. In order to cool the experimental slag (400 kg) it was poured to the ESR furnace mold (without adding the metal). After the cooling the whole slag disintegrated into powder (Figure 1).

a b

Fig.1 The view of slag bath in the mold of the 920 mm diameter after cooling (a) without metal remelting and after ingot melting (b).

The analogous result was achieved after the melting of the experimental solid ingot of 920 mm in diameter. The melting time was 5 hours.

A new slag does not require its removal and provides a good quality of ingot surface (figure 2).

Fig. 2 The view of surface of 920 mm diameter ingot.

The ingot is available for deformation (rolling, forging) without additional preparation of the surface which significantly increases the technological and economical properties of hollow ingots manufacture.

Further research of allowable limit of components content which provides a stable effect of self-disintegration, physical and technological properties of slag for the melting of hollow ingots is continued.

6. Conclusion

The analysis of modern practice of ESR furnace operation, the results of theoretical and experimental research allowed distinguishing requirements to the slag, fulfilling of which increases the quality of metal ingots and economical properties of modern ESR processes.

It is justified that further specialization of ESR slag is necessary for the remelted materials and schemes of remelting to increase economical and technical properties of the process. The main problems were formulated the slag developers are facing. These are the creation of “long” slag hardening under the relatively wide range of temperatures, slag with lowered (to 100-200°C below solidus) temperature interval of melting, slag with small or zero content of fluoride, slag with easy removed skull.

On the basis of slag ANF-29 there was developed a new composition that provides a high quality ingot surface and slag skull disintegrated into powder after cooling, this is especially important for ESR producing long pipes and shells.

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