STUDIES OF CHANGES IN THE ACTIVITY OF DISSOLVED OXYGEN IN THE SIMULATION OF FERROMANGANESE FILTRATION

The article deals with the solution of an urgent problem related to the process of filtration refining of ferroalloys. Based on the data obtained, it was found that combining the filtration process with casting ensures the flow of refined melt directly into the mold cavity and partial or complete elimination of secondary oxidation. To identify the underlying mechanism of filtration refining, the interaction of liquid metal with the filter in its separate pore channel was simulated. The main technological parameters of the process under consideration are calculated and practically confirmed.

Key word: ferroalloys, refining, filtration, oxygen activity, substrate effect.

INTRODUCTION

The process of ferroalloy smelting is accompanied by significant contamination of the processed alloy with non-metallic inclusions. It is connected with to the higher multiplicity of slag than in steelmaking and the high concentration of elements in the alloy that have a strong affinity for gases. Metallographic studies show that ferroalloys contain the same inclusions as in steel, but in very larger quantities.

In addition, it should be taken into account that due to the low oxygen concentrations achieved during these processes, the chemical potential of oxygen in the metal (μ_{O2} or Po_2) becomes significantly lower than the chemical potential of oxygen in the phases in contact with the metal - the atmosphere, slag, and refractory lining. As a result, oxygen is transferred from these phases to the metal volume [1]. This process develops when the melt is kept in a container, but especially during the casting. In this case, the degree of oxidation depends on the size of the specific contact surface of the metal jet with the air atmosphere and the duration of this contact.

Thus, during the production and casting of ball-bearing and other steel grades, the content of oxygen and nitrogen in ingots is increased 1.5 to 2 times, which contributes to significant contamination of steel with inclusions. As noted by V. P. Luzgin [2], a characteristic feature of the secondary oxidation process is contamination of the refined metal with non-metallic inclusions,

unstable carbon monoxide of deoxidizers, and deterioration of mechanical and other service properties of the processed metal.

As a result of secondary oxidation, not only the oxygen content increases, but also its activity [3]. This indicates that a significant part of the oxygen entering the metal does not interact immediately with the deoxidizing element, that is, the melt is supersaturated with these elements, but the degree of saturation does not reach the value that ensures the formation of inclusions. The necessary saturation is created when the steel temperature decreases and is accompanied by the formation of secondary inclusions.

Combining the filtration process with casting ensures that the refined melt flows directly into the mold cavity and partial or complete elimination of secondary oxidation.

The mechanism of filtration refining of metal melts is not limited to the stated ideas that the refining effect of filtration is only the result of cleaning from the formed non-metallic particles that are in the metal in a suspended state. There are all objective prerequisites, including thermodynamic and kinetic ones, for effective purification of the melt from dissolved impurities by the mechanism called the substrate mechanism in this paper [3].

The thermodynamic process of homogeneous nucleation can occur at any $\alpha > 1$, but at its low values it is realized with low intensity. Therefore, the interaction of the deoxidizer and oxygen dissolved in the metal is delayed in time and, under the condition of continuous cooling of the melt in the ladle and during casting, it does not have time to reach an equilibrium state.

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At the same time, heterogeneous nucleation of the oxide phase in liquid steel occurs much easier and 10^{13}-10^{22} times faster. The activation energy of this process is significantly less than for homogeneous embryo formation.

With regard to the process of separation of the oxide phase from the melt under consideration, it can be written that the activation energy of its heterogeneous crystallization is equal to:

$$\Delta G_{het} = K \left[(\lambda_{RmOn} - \lambda_{hs}) / \lambda_{RmOn} \right]^2, \qquad (1)$$

ΔG_{het} – activation energy of heterogeneous formation of a new phase / J/mol;
K – proportionality coefficient / J/mol;
λ_{RmOn} and λ_{hs} – geometric parameters of the crystal lattices of the new phase and the finished heterogeneous substrate.

The closer the deoxidation product and the heterogeneous embryo are in nature, the smaller the difference between λ_{RmOn} и λ_{hs}, which means that the activation energy of the heterogeneous formation of a new phase is less. With the identity of the nature of the deoxidation product and the finished substrate, the latter essentially becomes a homogeneous embryo and $\Delta G_{het} = 0$. In this case, the supersaturation of the melt will be determined only by kinetic factors – the presence of a sufficient number of ready-made germ particles and the delivery to them of the melt components involved in its deoxidation reaction. In real melts, there are always particles of non-metallic inclusions suspended in it, acting as ready-made substrates. The deoxidation reaction can also be realized on the surface of the refractory lining of buckets. However, completely supersaturation of the melt is not eliminated even under these conditions, obviously due to the insufficient development of the surface of the finished substrates and the lining of the buckets, as well as the delay in the process of delivering deoxidizer and oxygen atoms to them.

The nonequilibrium of the melt with respect to the deoxidation reaction creates thermodynamic prerequisites for its filtration purification from dissolved oxygen. These prerequisites are based on the fact that the filter surface can act as a finished substrate: in this case, the deoxidation reaction is realized directly on the filter surface [4]. In this case, the filter material can participate in the deoxidation reaction, reducing the activity of the R_mO_n deoxidation product.

METHOD OF CONDUCTING THE EXPERIMENT

To identify the underlying mechanism of filtration refining, the interaction of liquid metal with the filter in its separate pore channel was simulated. For this purpose, a granular filter with sinuous channels of variable cross-section was presented as a filter with straight cylindrical channels. In this regard, cylindrical tubes made of refractory material were considered as the unit cell of the filter.

Dissolved oxygen was considered as the removable impurity. This choice was due to the fact that a reliable method was developed to determine its activity based on the use of oxidation sensors – solid-electrolyte oxygen-concentration elements [5]. Similar probes are developed to determine the activity of sulfur dissolved in the melt, but their reliability is still significantly lower than oxygen probes. The processes of oxide and sulfide formation proceed in a similar way, which means that if the efficiency of processing the melt with solid-phase adsorbents is proved by the example of purification from dissolved oxygen, it will also be adequate for refining the alloy from super equilibrium dissolved sulfur [6].

The determination of oxygen by the electromotive force method is based on the occurrence of an oxygen-concentration element immersed directly in a liquid metal by an electromotive force proportional to the logarithm of the activity (partial pressure) of oxygen in it.

The electromotive force of this oxygen-concentration element is determined by the Nernst equation:

$$E = \frac{R \cdot T}{2 \cdot F} \cdot \ln \frac{a_O^{cm.}}{a_O^X} \qquad (2a)$$

Or

$$E = \frac{R \cdot T}{4 \cdot F} \cdot \ln \frac{P_{O_2}^{cm.}}{P_{O_2}^X}, \qquad (2b)$$

Where T is the temperature / K;
E – electromotive force of the oxygen concentration of the elements / mV;
F – gaz constant, 8,313 J / K · mole;
R – electrochemical constant, 96 580 Coulomb / g-EQ;
$a_O^{cm.}, a_O^X$ – respectively, the oxygen activity in the reference electrode and in the analyzed liquid metal / % by weight;
$P_{O_2}^{cm.}, P_{O_2}^X$ – respectively, the partial pressure of oxygen in the reference electrode and in the analyzed liquid metal / PA.

The main component of the oxygen-concentration element is a solid electrolyte made of stabilized calcium oxide, magnesium or yttrium zirconium dioxide. The specified material was selected based on almost 100 % of its ionic (oxygen) conductivity.

The reference electrode is a substance with a known partial pressure of oxygen. Mixtures of Mo + 10 % (by weight) MoO_2 and Cr + 2-5 % (by weight) Cr_2O_3 is usually used as reference electrodes.

The partial pressure of oxygen in these reference electrodes for the Cr-Cr_2O_3 mixture is calculated by the equation:

$$P_{O_2} = 10^{(-\frac{39425}{T} + 8,94)}; \qquad (3)$$

and for a mixture of Mo-MoO_2 – by the equation:

$$P_{O_2} = 10^{(-\frac{27550}{T} + 7,38)}; \qquad (4)$$

Recalculation of values of P_{O_2} calculated from equations 3 and 4 to the corresponding values a_O^{cm} and substi-

tuting them in equation 1a allows you to get the calculation formula for the reference electrode from a mixture of Cr-Cr$_2$O$_3$:

$$a_O^X = 10^{4,62 - \frac{10,086\,\check{A} + 13580}{\acute{O}}}; \qquad (5)$$

and for the reference electrode from a mixture of Mo-MoO$_2$:

$$a_O^X = 10^{2,658 - \frac{10,086\,\check{A} + 5661}{\acute{O}}}. \qquad (6)$$

Molybdenum current collectors are used for removing the electric potential of the reference electrode and the analyzed melt.

Digital voltmeters, potentiometers, and other voltage meters with an upper measurement limit of at least 750 mV can be used as a secondary device for recording the electromotive force of oxygen-concentration elements.

It is advisable to use potentiometers with continuous recording of readings, such as KSP-4 with measurement ranges of 0-10 mV, 0-20 mV, etc. To extend the range of measured voltage, a voltage divider with a total resistance of 8 – 12 Om must be installed at the input of these devices.

When setting up the experiment, we assumed that at a constant temperature and unchanged composition of the metal, a change in the concentration of oxygen dissolved in it is equivalent to a change in its activity.

Thus, to determine the efficiency of deposition of harmful ferromanganese impurities on a solid-phase surface, when processing its melt with adsorbents, the activity of dissolved oxygen was measured by the electromotive force method.

RESULTS

Ferromanganese of the FeMn78 brand used as the object of research. The filter material was quartz and alund tubes, the melt temperature maintained at 1 300 ˚C.

Initially, the initial oxygen activity was determined, after which a package of refractory tubes of the same chemical composition with a sensor inside was injected into the melt at the same depth, followed by removal of the potentiogram. After the potentiometer readings stabilized (on the potentiogram – a straight line at one EMF value), the KSP-4 was turned off, and the sensor was lifted out of the melt.

According to the method of measuring the activity of dissolved oxygen in a metal melt [7], the following potentiograms of oxygen activity (E / mV) obtained in

Table 1 **Oxygen activity in ferromanganese before and after contact**

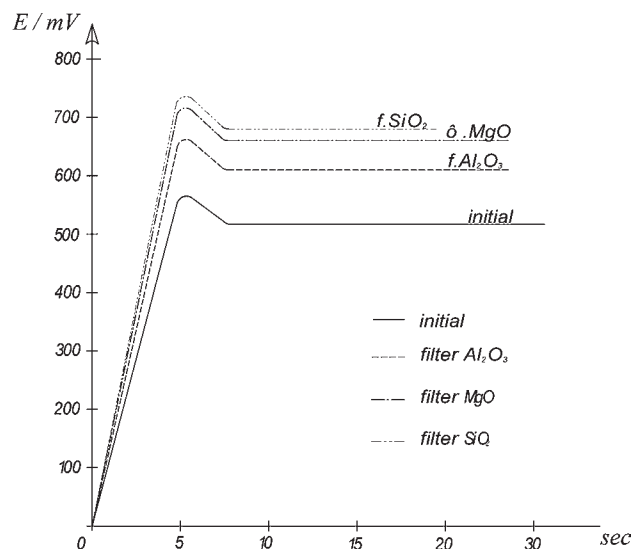| Meltdown options	Filter materials	E/ mV	ΔE/ mV	ΔE/ %
Initial	-	515	-	-
Filtered	Al$_2$O$_3$	610	+95	18,4
	MgO	660	+145	28,1
	SiO$_2$	680	+165	32,1

Figure 1 Influence of the filter material on changes in oxygen activity in ferromanganese

the initial ferromanganese and after contact of the melt with filters made of MgO, SiO$_2$ and Al$_2$O$_3$, shown in Figure 1 and Table 1.

CONCLUSIONS

The Table 1 above shows that the concentration of solute in oxygen steel in contact with filters made of MgO, SiO$_2$ and Al$_2$O$_3$ decreases by 28,1, 32,1 and 18,4%, respectively.

Thus, the existence of a substrate mechanism for refining from a dissolved impurity is proved experimentally on the model of a filter unit cell.

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Note: The translation of the N.M. Drag, Karaganda, Kazakhstan