A. D. MEKHTIYEV, ZH. D. ZHOLDUBAYEVA, B. D. ISSIN, V. N. GOLOVACHYOVA, A. V. YURCHENKO, D. K. ISSIN

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OXYGEN ACTIVITY CHANGING WHEN SIMULATING SILICON FILTERING PROCESS

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Preliminary Note – Prethodno priopćenje

In the article there is considered the efficiency of using filters for the refinement of metal melts, the use of filters in metallurgical practice and research of the inoculating mechanism of filter refinement of a metal melt from the dissolved impurities. In the inoculating mechanism the surface of the filter serves as a substrate for separation on it the nonmetallic phase directly from the melt, passing the stage of its separation into an isolated particle. This is proved experimentally, by monitoring the change of the deleted impurity activity by the EMF (electromotive force) method.

Key words: oxygen, activity, filter, silicon, nonmetallic phase

INTRODUCTION

The development of mechanical engineering and other metal-consuming branches in all countries predetermines various measures held by metallurgists for the purpose of increasing the purity of the made alloys. Silicon is widely used in different areas of engineering, medicine. It is an extremely important semiconductor material used for manufacturing microelectronic devices "chips" in the production of solar batteries. Silicon also finds broad application in instruments of medical purpose, for example, a TRIOMED instrument is successfully used in oncology (it helps to remove negative consequences of chemotherapy and removes ghost effects of radiation therapy, helps to protect the hematopoietic system). The use in the device of modern materials based on semiconductors of silicon and germanium permits to determine the dominating frequency that is radiated by cells with high accuracy and to carry out more "precisely" bioresonant diagnostics and therapy.

In connection with the aforesaid, much attention is paid to obtaining silicon of high purity that directly depends on the level of its refinement from impurities. At this the known technologies of refinement not always provide complex refinement from the dissolved and chemically bound impurities, they are ecologically unsafe (for example, chlorination). Therefore searching for new processes of refinement of technical silicon combining extra technical efficiency and ecological safety seems to be topical.

In this aspect the process of filter refinement of liquid metals which has actively been studied recently, is of interest and is industrially implemented into metallurgical practice (especially in foundry production). The technology of filter refinement of liquid metals is realized by passing a liquid metal through the pore flameproof device called a filter. When passing the liquid metal streams through the pore channels of the filter there are realized different mechanisms of refinement [1].

According to the modern representations [2] when filtering liquid metals the refining effect is caused by sedimentation on the filter surface of suspended in the melt nonmetallic particles, as well as separation of the nonmetallic phase directly from the melt [3].

Suspended nonmetallic particles can be arrested by the filter by the grid and adhesive mechanisms.

Alongside with grid and adhesive mechanisms in which implementation there is provided the melt refinement from chemically bound impurities in the form of nonmetallic particles, when filtering there is also realized the mechanism of the melt refinement from the over-equilibrium dissolved impurity. A necessary precondition of this is a thermodynamic ability of the impurity element P to enter a chemical reaction with any component of the alloy (K) at the filtering temperature, i.e. the possibility of running a reaction of the type:

$$x(K) + y(P) = (K_xP_y).$$

For theoretical assessment of the possibility of filter refining from the dissolved impurity there will be selected the element which is present practically in all metals and alloys, i.e. oxygen, and as the chemically active to it component there will be taken an R deoxidant. In general form the process of deoxidation is described by the reaction:

$$x(R) + y(O) = (R_xO_y),$$

A. D. Mekhtiev, Zh. D. Zholdubayeva, D. K Issin, V. N. Golovachyova, Karaganda State Technical University, Karaganda, Kazakhstan
A. V. Yurchenko, National Research Tomsk Polytechnik University, Tomsk, Rossia
B. D. Issin, L. N. Gumilyov Eurasian National University, Astana, Kazakhstan

as a result of which in the melt there is separated a corresponding oxide in the form of an independent nonmetallic phase.

The deoxidation reaction equilibrium in the real conditions by some kinetic reasons is not achieved. It means that though in the melt there are all thermodynamic conditions for separation of products of deoxidation in the independent phase, owing to the fast temperature drop when pouring the metal, the time deficit, as well as the deficit of germinal substrates for their crystallization, this opportunity does not manage to be realized completely. In other words, the melt super-saturation with components forming the nonmetallic phase (from the moment of the alloy smelting till its pouring in molds), is not completely eliminated.

In the course of the molten metal passing through the granular filter there is a repeated increase of the surface of contact between them due to the crushing of the melt into a set of small-sized streams which undergo sharp changes in the direction of the current. All this considerably intensifies and reduces the way of the deoxidant and oxygen delivery to the surface of the filtering elements, and, therefore, promote the origin on their surface of the nonmetallic phase by the heterogeneous mechanism.

The mechanism of filter refinement from an over-equilibrium dissolved impurity is called a substrate one, as the surface of the filter serves as a substrate for separation of the nonmetallic phase directly from the melt (Figure 1). For this purpose the deoxidant atoms [R] and oxygen atoms [O] are brought to the surface of the melt streams of the melt and when in contact with filter 2 on its surface there is realized the stage of separation of new nonmetallic phase 3 in the form of (R_xO_y) [4].

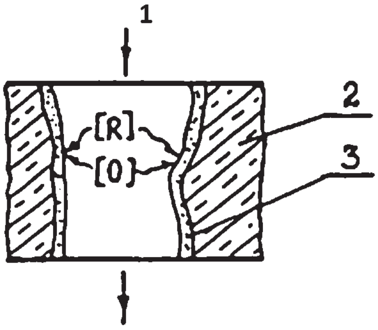


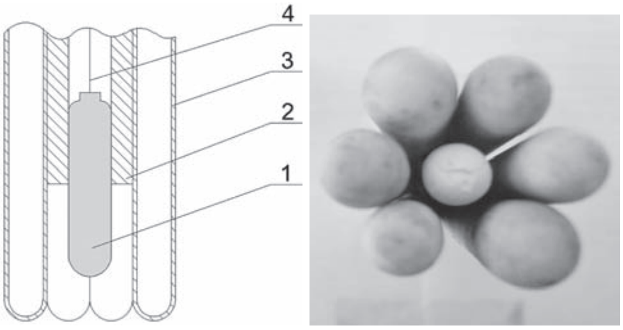
Figure 1 Substrate mechanism of liquid metals filter refining: 1 – liquid metal; 2 – filter; 3 – nonmetallic phase

The proof reality of liquid metals filter refining from the dissolved impurities by the substrate mechanism is changing oxygen activity in liquid silicon in filtering simulation.

METHODOLOGY OF STUDYING OXYGEN ACTIVITY IN SILICON MEASUREMENT

Measuring oxygen activity of oxygen by the EMF method is based on the origin in the oxygen-concentration element (other names: an activity meter, an oxidation sensor, an oxygen probe), dipped directly into the liquid metal, of electromotive force (EMF) proportional to the logarithm of activity (partial pressure) of oxygen in it [5].

When studying the mechanism of the metal melt filter refinement from the dissolved impurity there was originally simulated the process of the liquid metal interaction with the filter in its separate pore channel. For this purpose there was assembled a kind of an elementary cell of the filter (Figure 2) consisting of sensor round which there were densely laid down flameproof tubes that simulated the filter material. Under these conditions the thickness of the ring metal layer round the activity meter (δ) made 2,0…3,0 mm.



a b

Figure 2 Filter model cell: *a*) cell section, *b*) bottom view of the assembled cell: 1 - sensor; 2 - alundum tube; 3 - flameproof tubes; 4 - with molybdenum slip ring

When setting an experiment there was considered that at a constant temperature and invariable metal composition the change of oxygen concentration dissolved in it was equivalent to the change of its activity.

The set diagram for detecting the substrate mechanism of filter refinement is given in Figure 3.

The EMF values of the activity meter were fixed using a three-point potentiometer KSP - 4 with a scale division 5 mV alongside with measuring the melt temperature using a BP5/20 thermocouple. Under these conditions the fractional systematic error of indirect measurement of activity makes ± 5 %, and the intermittent error of determination does not exceed ± 8 %. Melting the furnace charge loaded in the alundum crucible (8) was realized in Tamman's furnace (6). Experiments were made in the inert atmosphere of argon. After melting the metal and achieving the required temperature which by means of the temperature sensor which was built in the set system was maintained constant within the experiment, into the melt to the fixed in advance depth by means of mechanism (4) there was entered oxygen probe (1) with slip ring (2) for measuring the initial activity of oxygen $E_{initial}$.

After that activity meter (1) was removed from the melt and to the same depth there was entered a heated-up model cell of filter (3) with the oxidation sensor with the subsequent reading of potentiogram E_f. The stable

EMF value fixed on potentiograms is set within 3…5 seconds after entering the sensor in the melt and, owing to the existence of a flameproof covering, is retained at this level for a long time [6].

Methodology of measuring oxygen activity in real filtering liquid metal

In case of real filtering unlike the simulation, a liquid metal was passed through the filtering device consisting of a casing made of a flameproof material restricting the volume of filtering elements from lateral surfaces and two ceramic grids with channel holes between which there was directly located granular filler. The control of changing oxygen activity when filtering the metal was exercised by mounting the oxygen-concentration elements immediately at once at the output of the metal melt from the filter or directly in the metal receiver.

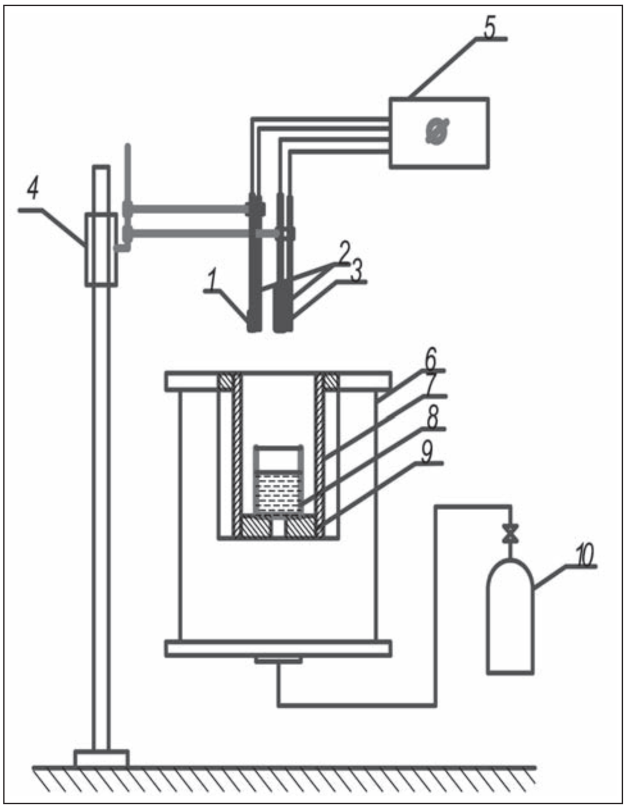


Figure 3 Set for fixation of oxygen activity changes in the melt when simulating the filtering process: 1 – activity meter; 2 – molybdenum collector; 3 – filter model cell with activity meter; 4 –mechanism of hoisting sensors and filters; 5 – KSP-4 potentiometer; 6 – Tamman's resistance furnace; 7 – heater; 8 – alundum crucible with metal; 9 – support; 10 – argon balloon

The bulk elements were used in the form of granules. For observing the equality of the pore channel dimension in the model cell and in the real filter there was preliminarily determined the needed diameter of these granules. It was started from that at the known thickness of the ring metal layer round the activity meter (as it was specified before δ =2,0…3,0 mm), the reduced size of this layer (R) will be equal to 1,0…1,5 mm. The same value there shall be a specified size of pore channels (R_{pc}) in the granular filter. As R_{pc} is connected to the diameter (D) of granules by the R_{pc}=0,31•D_{gr}/4 ratio, the granules shall have diameter: D_{gr} = 4 R_p / 0,31 = 4 (1,0 ÷ 1,5) / 0,31 = 12,9 ÷ 19,4 mm.

STUDYING THE FILTER MODEL MATERIAL ON THE SILICON REFINEMENT FROM DISSOLVED OXYGEN

For experimental assessment of the silicon refinement level from the dissolved oxygen by the above-stated method and on the set presented in Figure 3, there was simulated the process of liquid metal interaction with the granular filter in its separate pore channel. The object of studying served metallurgical silicon of the Ushtobe Silicon Plant. Its chemical composition is given in Table 1 served.

Table 1 **Chemical composition of metallurgical silicon *I wt, %***

Technical silicon variant	Si	Fe	Al	Ca
Unrefined	98,0	0,8	0,80	0,50
Refined	99,5	0,3	0,25	0,04

As a filter model there originally was used quartzite tubes. In the work there was used a the three-point electronic potentiometer KSP-4 permitting to pick up and to register signals of the oxygen probe in the range from 0 to 1 000 mV, as well as a thermocouple. Under these conditions the fractional systematic error of indirect measurements of activity made ± 5 %, and the intermittent error of determination did not exceed ± 8 %.

In Figure 4 there are given potentiograms of the EMF (E, mV) continuous measurement in liquid silicon before the melt contact with the models of SiO_2 filters.

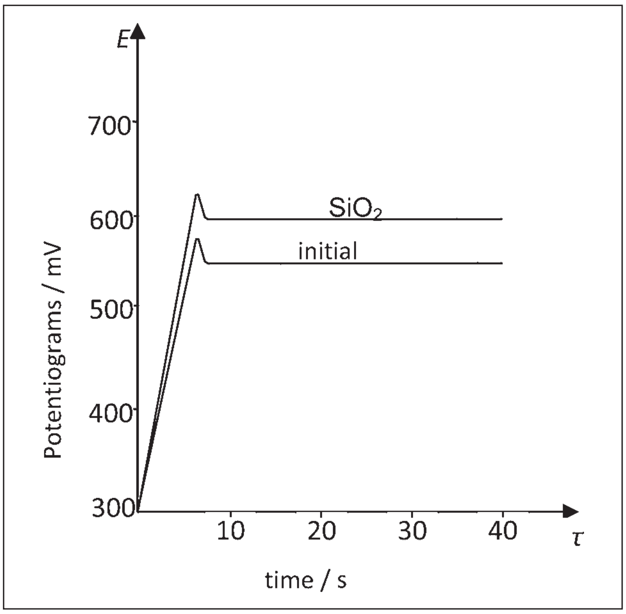


Figure 4 Potentiograms of the oxygen sensor EMF in liquid silicon before and after the melt contact with SiO_2 filter

Table 2 **Oxygen activity values in liquid silicon before and after introducing the model of filtering cell in the melt**

Variant	Filter material	EMF of the oxygen sensor E / mV	
		E,	$\Delta E = E_{fil.} - E_{unfil.}$
Unfiltered	–	550	–
Filtered	SiO_2	600	+ 50

In the initial melt of technical silicon, according to the obtained results, the EMF of the oxygen sensor makes ~ 550 mV. In comparison with the initial, when introducing in the melt a quartzite cell of the filter, the EMF value is steadily increased by 50 mV (Table 2).

Statistical processing of the obtained data showed that the EMF measurements were performed with identical accuracy and the mean values differ naturally in them.

The results of measuring the oxygen activity changes in liquid silicon before and after introducing in the melt the model of the filtering cell given in Table 2, show that in simulation of silicon filtering through a SiO_2 filter, the EMF value of the oxygen sensor E increases from 550 to 600 mV. It specifies that in liquid silicon the oxygen potential decreased that is equivalent to the lowering of the dissolved oxygen concentration in it. A considerable difference in the EMF values in “non-filtered” and “filtered” variants ($\Delta E = 50$ mV) is the experimental proof of the silicon refinement effect from the dissolved oxygen and is explained by the involvement of the filtering material as a heterogeneous substrate in the course of separation an oxide-coated phase on it [6].

CONCLUSIONS

When filtering liquid steel by the measured EMF values of the oxygen sensor there can be calculated oxygen activity by the formula:

$$\mathrm{Iga}_{[O]} = 2{,}685 - \frac{10{,}087\ E + 5660}{T}$$

where $a_{[O]}$ is activity of the dissolved oxygen, mass / %;

E is the EMF value of the activity meter / mV,

T is the melt temperature / К

At this the difference in the EMF values is directly translated into the difference of oxygen activities and, respectively, into the difference of concentration of the dissolved oxygen.

In case of silicon owing to the absence of formulas for calculation of oxygen activity $a_{[O]}$ for the EMF value of the oxygen sensor E such assessment cannot be carried out. It is possible to claim only qualitatively that there is reduces the dissolved oxygen concentration in liquid silicon when filtering. Therefore, on the surface of the filter channels there is realized the reaction of chemical binding the dissolved elements-impurities by the dissolved oxygen, i.e. there acts the substrate mechanism.

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