



METHODS OF CONTROL OF SILICON OXIDE ACTIVITY IN SLAG MELTS

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Silicon oxide is included into composition of fluxes for welding of carbon and low-alloy steels. To predict the metallurgical and welding-technological properties of fluxes, it is important to know their activity in slag melt. The aim of the present work is to develop the methods of in-process evaluation of activity (effective concentration) of silicon oxide SiO₂ in slag melts and to define the methods of its control. The design of unique electrolytic sensor has been developed. The application of alloy, containing 5 wt.% Si as the second electrode allowed increasing the heat resistance of the sensor up to 1500 °C. Using the designed sensor, the procedure was suggested for determination of SiO₂ activity in slag melts by using the method of electromotive forces, which guarantees the accuracy in measurement of electromotive forces within 1–2 mV ranges. This procedure can be applied in metallurgy directly in the melting process, as well as in the development of welding consumables. It was found that increase in MgO content in slag melt of MgO–Al₂O₃–SiO₂–CaF₂ system causes the reduction in silicon oxide activity, that can be explained by the formation of refractory and thermodynamically stable silicates and aluminates of magnesium. The effect of additions (1 wt.%) of metals on the SiO₂ activity in melts of MgO–Al₂O₃–SiO₂–CaF₂ system was determined. The feasibility of control of thermodynamic activity of silicon oxide in slags in welding and, respectively, the processes of silicon reduction and formation of non-metallic inclusions in welds is shown. 5 Ref., 3 Tables, 1 Figure.

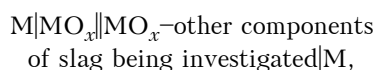
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The oxide and oxide-fluoride melts are widely used in metallurgy and welding. To predict the metallurgical and technological properties of slags in molten state, it is important to know their thermodynamic properties, in particular the activity of components of slag melts. The main component, included into composition of fluxes for welding of carbon and low-alloy steels, is silicon oxide. It is this component that defines the degree of polymerization of melt and, respectively, its structurally dependent properties. The complex of these properties defines the technological parameters of fluxes in the process of welding. At the same time, the presence of silicon oxide in the flux composition is a cause of proceeding of a number of redox reactions during welding, such as silicon reduction and formation of silicate non-metallic inclusions, non-desirable from the point of view of producing the optimum microstructures and mechanical properties in welding of advanced high-strength low-alloy steels. The advanced welding consumables are, as a rule, complex multi-component systems. Moreover, not only the melt components have

an influence on the activity of slag melt components during welding, but also metals, included into composition of steel, wire and flux.

The aim of the present work is to develop the methods of in-process evaluation of activity (effective concentration) of silicon oxide SiO₂ in slag melts and to define the methods of its control.

The most accurate method of determination of activities of components in alloys is the method of electromotive forces (EMF) [1]. Its principle is as follows: to investigate the activity of one of components of oxide systems, a concentration element is developed without transfer of ions of the type



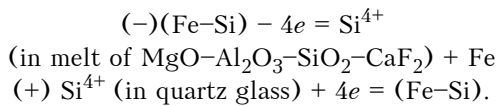
where M, MO_x are the metal and lower oxide of this metal. The developed concentration element for measurement of activity of silicon oxide SiO₂ in melt of MgO–Al₂O₃–SiO₂–CaF₂ system [2] is written schematically as follows:



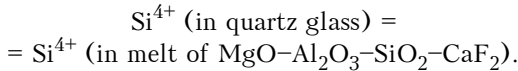
where (–) and (+) are the negative and positive poles.



In operation of this concentration element the following processes are proceeding at the electrodes:



Common process:



Activity of SiO_2 was calculated using the known equation

$$E = RT/4F \ln a_{\text{SiO}_2}/a_{\text{SiO}_2}^{\text{fl}}$$

where E is the EMF of concentration element; R is the gas constant; a_{SiO_2} , $a_{\text{SiO}_2}^{\text{fl}}$ are the activities of silicon oxide SiO_2 , respectively, in quartz glass and liquid glass of $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-CaF}_2$ system.

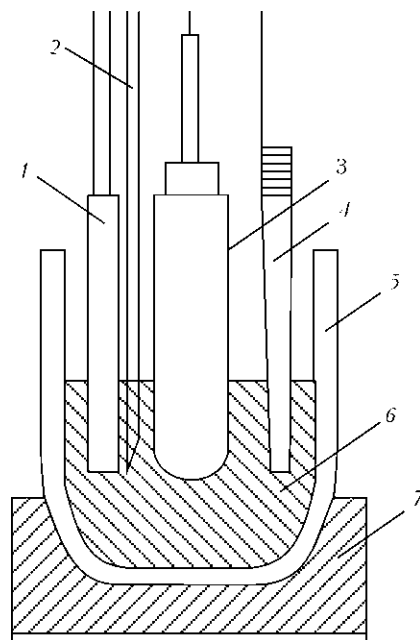
At $T = 1673 \text{ K}$ $E = -0.036 \ln a_{\text{SiO}_2}^{\text{fl}}$, hence $a_{\text{SiO}_2}^{\text{fl}} = e^{-E/0.036}$.

This cell can be manufactured in the following way. In a graphite block two depressions are drilled for electrode of Fe-Si (ferrosilicon). From the bottom or on the side the tungsten current taps are connected. The cell in this form is heated up to $1500 \text{ }^\circ\text{C}$ in inert atmosphere and subjected to holding for 30–60 min. The fused ferrosilicon will have a good contact with current taps and walls of depressions. Then, a quartz glass is poured on the surface of one Fe-Si electrode, the slag being investigated is poured on the second electrode surface. Determination of SiO_2 activity by using this procedure is a complex task. Moreover, during the experiment the interaction of oxides and Fe-Si with graphite takes place. In this connection the need arises in its replacement by other more inert materials, such as boron aluminonitride.

Therefore, the task was put forward to design a unique electrolytic sensor for in-process determination of SiO_2 activity in oxide and oxide-fluoride melts. Special electrodes were manufactured, which had at the beginning the pure Si, SiC or MoSi_2 as a Si-containing component. It was found during special experiments that a double electrical layer is slowly formed on the surfaces of SiC and MoSi_2 , as the silicon is strongly bonded with other atoms of carbon or molybdenum. Sensor with electrode of pure silicon as a metallic component allowed making measurements only up to $1400 \text{ }^\circ\text{C}$. Therefore, basing on the state diagram of Fe-Si system the alloy was

selected by us, containing 5 wt.% Si and melting at temperature of $1500 \text{ }^\circ\text{C}$, and also the ferrosilicon-containing electrodes were manufactured using the technology described below. The fine-grain crushed silicon was mixed with powdered carbonyl iron of OSCh grade and poured into a quartz ampoule of 5 mm diameter and 4 cm length. Then, the tungsten rod of 40–50 cm length was put into this mixture. The junction was sealed with a paste of aluminium oxide and liquid glass to provide the more quality contact between the tungsten rod and alloy and to increase the junction strength. The second electrode of the concentration element represented a rod of ferrosilicon (5 wt.% Si), fastened to the tungsten current tap by a thin molybdenum wire. For this, a groove was cut in the electrode upper part by a diamond disc to insert the 1 mm diameter tungsten wire. The place of junction was pasted by a mixture of a powdered aluminium oxide with liquid glass. The tungsten current taps were insulated by inserting them into porcelain tubes. Electrodes were isolated one from another by a corundum plate and tied by a molybdenum wire. Scheme of the concentrated element, which was used for in-process determination of SiO_2 activity in oxide and oxide-fluoride melts, is given in the Figure.

The slag being investigated (8 g mass) was poured into a corundum round-bottomed crucible which was placed into the Tamman furnace. After



Scheme of a concentration element: 1 – thermocouple VR5-20; 2 – mixer; 3 – rod of Fe-Si connected with tungsten current tap in case of SiO_2 ; 4 – rod of Fe-Si connected with tungsten current tap; 5 – corundum crucible; 6 – slag being investigated; 7 – support of niobium plate and boron aluminonitride

**Table 1.** Activity of SiO₂ in model slags of MgO–Al₂O₃–SiO₂–CaF₂ system

SiO ₂ , wt.%/mole fraction	Al ₂ O ₃ , wt.%/mole fraction	CaF ₂ , wt.%/mole fraction	MgO, wt.%/mole fraction	E, mV	a _{SiO₂} , mole %
40/0.507	40/0.298	20/0.195	0/0	20	0.573
38/0.462	38/0.272	19.2/0.179	4.8/0.087	47	0.270
36/0.418	36/0.246	18/0.161	10/0.174	49	0.250
34/0.380	34/0.223	17/0.146	15/0.251	75	0.123

heating up to 1400 °C it was subjected to holding for 3–5 min at this temperature (for homogenization). Then, two electrodes, above-described, were immersed slowly into the melt. After heating of electrodes up to preset temperatures the value of EMF was preserved constant within 1–2 mV ranges.

The accuracy and propriety of the developed procedure were checked on slags of CaO–SiO₂ system, well-studied earlier. It was occurred that activities of SiO₂, determined by us, are correlated with literature data within the errors of experiment [2]. This gave the grounds to start the determination of activity of silicon oxide SiO₂ in model slags of MgO–Al₂O₃–SiO₂–CaF₂ system, to which a whole number of fluxes for welding of high-strength low-alloy steels is referred. The developed procedure was applied for investigation of dependence of MgO effect on SiO₂ activity. The obtained results are given in Table 1.

It is seen from Table 1 that the MgO adding into slags of MgO–Al₂O₃–SiO₂–CaF₂ system causes a significant decrease of silicon oxide activity. This can be explained by the formation of complex compounds close by composition to Al₂MgO₄ and Mg₂SiO₄ [3], which are very refractory and thermodynamically stable.

During welding the components of fluxes are coming into interaction with alloying elements, included into composition of electrode wire and steel. In addition the agglomerated fluxes, as a rule, contain the alloying elements. To study this interaction, the powdered alloys in the amount of 1 wt.% of ferrosilicon FS75 (75 wt.% Si),

Table 2. Effect of additions of ferroalloys and metal manganese on SiO₂ activity in melt

Melt	E, mV	a _{SiO₂} , mole %
Flux	75.5	0.123
Flux + Fe–Mn	114.0	0.042
Flux + Mn	141.7	0.020
Flux + Fe–Si	161.0	0.011
Flux + Fe–Ti	277.5	0.001
Flux + Ca–Si	332.5	0.0001

ferrotitanium FTi70 (70 wt.% Ti), silicocalcium SK30 (30 wt.% Ca), ferromanganese FMn90 (90 wt.% Mn) and metal manganese Mn998 (99.8 wt.% Mn) were added to the oxide fluoride melt (34 wt.% SiO₂, 34 wt.% Al₂O₃, 17 wt.% MgO, 15 wt.% CaF₂) using a cup with a corundum tube.

The results of measurements of EMF, obtained by using the above-described procedure, and appropriate values of activity of silicon oxide in slag melt are given in Table 2. It is seen from Table 2 that the activity of SiO₂ in melt of MgO–Al₂O₃–SiO₂–CaF₂ system with adding of ferroalloys is decreased. This can be explained by reaction proceeding between SiO₂ and metals.

To explain the effect of different metals on SiO₂ activity in the studied oxide melt, the thermodynamic probability of these processes was evaluated. For this, the change of Gibbs energy ΔG for each reaction given below (at 298 and 1673 K) was calculated:

1. [Mn] + (SiO₂) → (MnO₂) + [Si]
2. 3[Mn] + 2(SiO₂) → (Mn₃O₄) + 2[Si]
3. 2[Mn] + (SiO₂) → 2(MnO) + [Si]
4. 4[Ti] + 3(SiO₂) → 2(Ti₂O₃) + 3[Si]
5. [Ti] + (SiO₂) → (TiO₂) + [Si]
6. 2[Fe] + (SiO₂) → 2(FeO) + [Si]
7. 4[Fe] + 3(SiO₂) → 2(Fe₂O₃) + 3[Si]
8. 3[Fe] + 2(SiO₂) → (Fe₃O₄) + 2[Si]
9. [Si] + (SiO₂) → 2{SiO}
10. 2[Ca] + (SiO₂) → 2(CaO) + [Si],

where (), [], { } are the liquid, solid or gaseous state of substances.

To calculate ΔG at 298 K the following formula was applied:

$$\Delta G = \sum_i v_i(\Delta G_i)_{\text{form}}^{\text{prod}} - \sum_i v_i(\Delta G_i)_{\text{form}}^{\text{reag}}$$

Thus, for reaction 1 we have

$$\Delta G_{298}^0 = \Delta G_{\text{MnO}_2, 298}^0 + \Delta G_{\text{SiO}_2, 298}^0 - \Delta G_{\text{Mn}, 298}^0 \quad (1)$$

To calculate ΔG at 1673 K, we assume in the first rough approximation that ΔC_p = 0. Then, the change of Gibbs energy for temperature 1673 K is equal to



Table 3. Calculated thermodynamic functions for reactions of metals with SiO₂

Number of reaction	ΔH_{298}^0 , kJ/mole	ΔS_{298}^0 , kJ/mole	ΔC_p , kJ/mole	ΔG_{298}^0 , kJ/mole	ΔG_{1673}^0 , kJ/mole (I approx.)	ΔG_{1673}^0 , kJ/mole (II approx.)
1	337	-2.55	2.14	333.91	332.76	329.91
2	329	42.85	46.49	310.22	257.38	319.37
3	87.9	33.08	7.76	64.70	32.57	42.913
4	-463	-35.38	17.50	-471.90	-403.90	-380.60
5	-83	-3.97	4.36	-85.59	-76.68	-70.87
6	325	29.74	23.76	305.42	275.13	306.81
7	929	-0.46	31.60	913	930.22	972.35
8	598	17.26	23.37	666.99	568.97	600.13
9	635	351.10	15.57	524.35	47.16	67.92
10	-363	-25.38	7.50	-3316	-303.90	-280.60

$$\Delta G_{1673}^0 = \Delta H_{298}^0 - T\Delta S_{298}^0. \quad (2)$$

To calculate the change of enthalpy of reaction 1 the following formula is applied:

$$\Delta H_{298}^0 = \sum_i v_i(\Delta H_{298}^0). \quad (3)$$

For reaction 1 this formula acquires the form

$$\Delta H_{298}^0 = \Delta H_{MnO_2, 298}^0 + \Delta H_{Si, 298}^0 - \Delta H_{SiO_2, 298}^0 - \Delta H_{Mn, 298}^0, \quad (4)$$

where $\Delta H_{MnO_2, 298}^0$, $\Delta G_{MnO_2, 298}^0$ are the enthalpy and Gibbs energy of MnO₂ formation.

Similarly for change of entropy of given reaction

$$\Delta S_{298}^0 = S_{MnO_2, 298}^0 + S_{Si, 298}^0 - S_{SiO_2, 298}^0 - S_{Mn, 298}^0. \quad (5)$$

Equation (2) gives the accurate enough results within wide range of temperatures. However, in many cases this is stipulated not by the fact that ΔH and ΔS are slightly depended on temperature, but a partial mutual compensation of effect of changes of these functions.

In the second approximation (Uhlich) the temperature dependence of thermodynamic functions is taken constant, i.e. the change of heat capacity of products and reagents of reaction ΔC_p is constant and equal to change of heat capacity of all the substances at room temperature:

$$\Delta G_T^0 = \Delta H_{298}^0 - T\Delta S_{298}^0 + \Delta C_p \cdot 298(T - 298 - T \ln T/298). \quad (6)$$

As it is not important for us the precise value ΔG , but its sequence and sign, we shall apply the approximated methods of calculation of ΔG using equations (2) and (6). When calculating, the literature data were used [4]. The data for manganese were taken for α -form, stable under

normal conditions. The results of calculations are given in Table 3.

For reactions 4, 5 and 10, ΔG_{1673}^0 is negative. This proves the interaction of titanium and calcium with SiO₂, moreover, the proceeding of reactions 4 and 10 is more probable. This is well correlated with experimental data, obtained by us, on decrease of SiO₂ activity at adding the ferrotitanium and silicocalcium into slag melt of MgO–Al₂O₃–SiO₂–CaF₂ system. Results of calculations of Gibbs energy, given in Table 3, confirm that titanium and calcium, included into composition of ferroalloys, interact with silicon oxide by the above-mentioned scheme. To explain the decrease in SiO₂, obtained experimentally at adding of other ferroalloys, it is necessary to use during calculation the partial molar Gibbs energies of metals, accounting for their activity, as well as the fact that when contacting the slag these metals are in a molten state. For this, we shall apply the modified equation

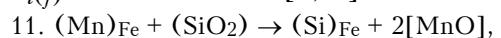
$$\Delta G = \sum_i a_i v_i (\Delta G_i)_{\text{form}}^{\text{prod}} - \sum_i a_i v_j (\Delta G_j)_{\text{form}}^{\text{reag}}, \quad (7)$$

where ΔG_i , ΔG_j are the partial molar Gibbs energies of components of final and initial melts.

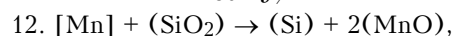
In its turn

$$\Delta G_{i(j)} = RT \ln a_{i(j)}. \quad (8)$$

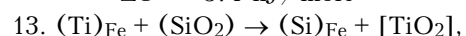
Activities of components of ferroalloys and slags $a_{i(j)}$ were used from [1, 5]:



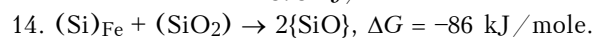
$$\Delta G = -460 \text{ kJ/mole}$$



$$\Delta G = -371 \text{ kJ/mole}$$



$$\Delta G = -878 \text{ kJ/mole}$$



The values of Gibbs energies of reactions 11–14 are negative, thus proving their self-proceed-



ing in a straight direction. This is well correlated with data, according to which the activity of SiO_2 is significantly decreased at adding of the mentioned ferroalloys into the slag being investigated.

Therefore, with adding of some metals into complex oxide melts it is possible to control the activity of its components, in particular SiO_2 and, thus, the metallurgical properties of flux during welding. With decrease of SiO_2 in slag melt it is possible to suppress the proceeding of reactions of silicon reduction and formation of silicate non-metallic inclusions, undesirable from the point of view of metallurgy of low-alloy steel welding.

Conclusions

1. Activities of SiO_2 in slag melts of $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{CaF}_2$ system were determined by the EMF method using the designed electrolytic sensor.

2. It was found that the increase in MgO content in slag melt of $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{CaF}_2$ system causes the decrease in activity of the silicon oxide, that can be explained by the formation of

refractory and thermodynamic stable silicates and aluminates of magnesium.

3. The effect of additions of metals on SiO_2 activity in melts of $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{CaF}_2$ system was studied. It was found that adding of 1 % of silicocalcium, ferrotitanium, ferrosilicon, ferromanganese and metal manganese into melt of $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{CaF}_2$ system leads to the jumpy drop of silicon oxide activity. The highest decrease (by 2–3 orders) is attained at adding of silicocalcium and ferrotitanium.

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NEWS

Trenchless Laying of Pipelines

The principle of trenchless well driving consists in the use of compressed air to provide a reciprocal movement of the pneumatic hammer striker, whose impact on the casing is transferred to a reamer to cause an axial movement of the latter. A series of machines of this type were developed for punching of holes with a diameter of up to 630 mm.

For trenchless replacement of pipes, a special reamer is mounted on the impact mechanism (pneumatic hammer) located in the working well. This reamer provides destruction of an old pipe and expansion of soil to match its external diameter. A new pipeline, which is lengthened by sections from the working well, is pulled into the formed channel in movement of the reamer. The possibility exists of the continuous feed of a one-piece spiral-welded pipe made in site (in the well) from strip-type polyethylene billets. The reamer and a new pipe are pulled by using a cable and hoist from the receiving well. Length of a replaced section is up to 50 m.

Application:

- making of through, blind horizontal, inclined and vertical passages in puddled soils (e.g. in street or road intersections, etc.);
- trenchless replacement of old brittle material sewer pipes by polyethylene ones;
- removal of failed service lines from earth;
- installation of concrete and reinforced concrete grouted piles, cleaning of functioning service lines.

The trenchless technology allows several times saving of the funds, compared to traditional trench laying of pipelines, and preserves the outward appearance of territories within the work zone (this is particularly important for big cities with heavy traffic, and for reconstruction or overhaul of active underground service lines in urban development areas).

The speed of laying of a new pipeline is 6 m/h at a diameter of plastic pipes of 225 or 315 mm.

Vibrations of earth in trenching are similar to those occurring in foundation piling, i.e. they are not in excess of those specified by standards.