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THERMODYNAMIC CALCULATION OF COMPLEX DEOXIDATION BY ALUMINUM AND SILICON OF MELTS OF STEEL 20GL FOR CAST PARTS OF ROLLING STOCK AUTOCOUPLE DEVICES

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Abstract

This article is devoted to the method of calculating the joint complex deoxidation of steel grade 20GL. Steel grade 20GL was chosen as the metal under study. Improving the operational reliability and increasing the mechanical properties of castings made of 20GL steel is an urgent task today, which leads to a reduction in the cost of their manufacture. Such a complex problem can be solved in different ways. One of them is the improvement of steel deoxidation technology.

Keywords: Steel 20GL; complex deoxidation; oxygen activity; thermodynamics; aluminum; silicon.

1.Introduction

The operating conditions of wagons in the future will be characterized by an increase in the weight of freight trains up to 10–12 thousand tf with a train length of 1200–1300 m, an increase in the number of wagons with a gross weight of up to 176 tf, an increase in the efficiency of brakes in the train, an increase in the average velocities of collision of wagons, etc. n. For normal operation in such operating conditions, the automatic coupling equipment of cars must have appropriate strength, increased energy consumption, the necessary absorbing capacity and the optimal shape of the power characteristic.

In order to increase the strength of automatic coupling equipment, the industry is switching to the manufacture of its main parts (automatic coupler body, traction clamp, elements of the clutch mechanism, stops, etc.) from high-strength steels, in particular alloyed with vanadium and manganese. The mechanical properties of these steels are significantly higher than the corresponding properties of steels currently used for the manufacture of the same parts of an automatic coupler . Research continues on other even stronger steels and methods for manufacturing the main and most critical parts of automatic coupling equipment.

Simultaneously with the use of alloyed steels for the production of automatic coupler parts , design studies are underway to strengthen its elements and assemblies. So, in recent years, reinforced front and rear stops, a traction collar and an automatic coupler body have been introduced into production. The automatic coupler is reinforced by the introduction of four ribs in the shank, an increase in the wall section, a change in the design of the large tooth ribs, etc. All this (along with the use of low-alloy steel made it possible to increase the breaking force of the automatic coupler. In order to improve the quality of automatic couplers in general and its components and parts Separately, in industry, the technology of their production is constantly being improved.

This is achieved by complex mechanization and automation of the processes for manufacturing parts and assemblies of the automatic coupler .

Therefore, both an increase in the quality indicators of castings from 20GL steels and a reduction in the cost of their manufacture are topical. Such a complex problem can be solved in different ways. One of them is the improvement of the technology of deoxidation and modification of steel.

Qualitative deoxidation involves the treatment of steel with the minimum required amount of deoxidizer .

The technology for smelting 20GL steels also necessarily includes final deoxidation and modification of the melt in the ladle. As a rule, aluminum is used for this. At the same time, it is important to ensure the optimal residual content of this element. The instability of aluminum assimilation makes it difficult to prevent this process . As an alternative, complex deoxidation with silicon and aluminum was considered.

2. Methods

Thermodynamic calculations of complex deoxidation by silicon and aluminum. A detailed thermodynamic calculation of the options for deoxidation of steel 20GL with the composition shown in Table 1 was carried out. The metal composition adopted for research and for thermodynamic analysis corresponds to (GOST 22703-2012).

Table 1 - Chemical composition of steel grade 20GL, % (wt.)

C	Mn	Si	S	P	Cr	Cu	Ni	Al	V
0.2 2 0	1.25	0.365	0.020	0.025	0.096	0.085	0.097	0.027	0.021

The steel deoxidation reaction can be represented in the following general form :

$$x[R] + y[O] \leftrightarrow R_xO_y \qquad (1)$$

$$K_p(T) = \frac{a_{R_xO_y}}{a_R^x \cdot a_O^y} \qquad (2)$$

The solubility of oxygen in 20GL steel deoxidized according to reaction (1) was calculated from the expression of the equilibrium constant.

$$K_p = \frac{\left(a_{R_xO_y}\right)}{[a_R]^x \cdot [a_O]^y} = \frac{\left(a_{R_xO_y}\right)}{[R]^x \cdot f_R^x \cdot [O]^y \cdot f_O^y} \qquad (3)$$

In the case of complex deoxidation of a metal melt, the activity of oxides formed as a result of the deoxidation process is less than unity, due to this, with the same content of the deoxidizing element, it is possible to obtain a metal with a lower oxygen concentration [1]. In complex deoxidation , the deoxidation products - oxide solutions - melt at lower temperatures than pure oxides, which makes it possible for them to coagulate and more completely remove steel from the melt.

For deoxidation of 20GL steel, it is possible to use such complex deoxidizers as silicocalcium , silicobarium , aluminum and silicon, and it is also possible to use complex multicomponent ligatures containing all of these elements. To calculate the complex deoxidation of steel 20GL, the method previously described in the literature

[1–5] was used. Deoxidizers in the metal melt, reactions of interaction with oxygen can be written for each:

$$n \cdot [R^{!}] + m \cdot [O] = R^{!}_{n}O_{m} \tag{4}$$

$$k \cdot [R^{!!}] + p \cdot [O] = R^{!!}_{k}O_{p} \tag{5}$$

In this case, the activities of the reaction products will be less than unity, and due to this, with the same content of the deoxidizer element , a lower oxygen concentration in the melt can be obtained than with the separate introduction of each deoxidizer into the metal.

The equilibrium constants for the reaction (4) and (5) are expressed through the following equations

$$K_{R^{!}} = \frac{a_{R^{!}_{n}O_{m}}}{a^{n}_{R^{!}} \cdot a^{m}_{O}} = \frac{a_{R^{!}_{n}O_{m}}}{f^{n}_{R^{!}} \cdot [R^{!}]^{n} \cdot f^{m}_{O} \cdot [O]^{m}} \tag{6}$$

$$K_{R^{!!}} = \frac{a_{R^{!!}_{k}O_{p}}}{a^{k}_{R^{!!}} \cdot a^{p}_{O}} = \frac{a_{R^{!!}_{k}O_{p}}}{f^{k}_{R^{!!}} \cdot [R^{!!}]^{k} \cdot f^{p}_{O} \cdot [O]^{p}} \tag{7}$$

where $a_{R^{!}_{n}O_{m}}$, $a_{R^{!!}_{k}O_{p}}$ are the activities of the reaction products;

$[R^{!}]$, $[R^{!!}]$, $[O]$ are mass contents of deoxidizing elements and oxygen, respectively;

$f_{R^{!}}$, $f_{R^{!!}}$, f_{O} are the Henry activity coefficients of deoxidizing elements and oxygen, respectively;

n , m , k , p are stoichiometric coefficients.

In the joint deoxidation of the melt by two elements $R^{!}$ and , $R^{!!}$ the stronger deoxidizer takes predominant part in the reaction $R^{!}$, however, if complex oxide compounds are obtained in the process $xR^{!}_{n}O_{m} \cdot yR^{!!}_{k}O_{p}$, this contributes to the participation of a weaker deoxidizer in the reaction $R^{!!}$. The formation reaction of a complex oxide compound $xR^{!}_{n}O_{m} \cdot yR^{!!}_{k}O_{p}$ can be written in the following form.

$$xR^{!}_{n}O_{m} + yR^{!!}_{k}O_{p} = xR^{!}_{n}O_{m} \cdot yR^{!!}_{k}O_{p} \tag{8}$$

The equilibrium constant for reaction (8) has the following form

$$K_{R^{!}R^{!!}} = \frac{a_{xR^{!}_{n}O_{m} \cdot yR^{!!}_{k}O_{p}}}{a^{x}_{R^{!}_{n}O_{m}} \cdot a^{y}_{R^{!!}_{k}O_{p}}} \tag{9}$$

If the resulting complex oxide $xR^{!}_{n}O_{m} \cdot yR^{!!}_{k}O_{p}$ is the only one, then its activity $a_{xR^{!}_{n}O_{m} \cdot yR^{!!}_{k}O_{p}}$ is assumed to be unity, and equation (9) takes the form

$$K_{R^{!}R^{!!}} = \frac{a_{xR^{!}_{n}O_{m} \cdot yR^{!!}_{k}O_{p}}}{a^{x}_{R^{!}_{n}O_{m}} \cdot a^{y}_{R^{!!}_{k}O_{p}}} = \frac{1}{a^{x}_{R^{!}_{n}O_{m}} \cdot a^{y}_{R^{!!}_{k}O_{p}}} \tag{10}$$

From the prologarithmic equations for the equilibrium constants (6) and (7) for reactions (4), (5) it is possible to determine the dependence of the oxygen activity in the melt on the concentration of each deoxidizer .

$$lg(f_O\cdot[O])_{R^!}=\frac{1}{m}\cdot\left(lg\,a_{R^!_nO_m}-lg\,K_{R^!}-n\cdot lg(f_{R^!}\cdot[R^!])\right)\qquad(11)$$

$$lg(f_O\cdot[O])_{R^{!!}}=\frac{1}{p}\cdot\left(lg\,a_{R^{!!}_kO_p}-lg\,K_{R^{!!}}-k\cdot lg(f_{R^{!!}}\cdot[R^{!!}])\right)\qquad(12)$$

In the case of joint complex deoxidation by both deoxidizers , the oxygen activities determined by equations (11) and (12) are equal.

$$\frac{1}{m}\cdot\left(lg\,a_{R^!_nO_m}-lg\,K_{R^!}-n\cdot lg(f_{R^!}\cdot[R^!])\right)=\frac{1}{p}\cdot\left(lg\,a_{R^{!!}_kO_p}-lg\,K_{R^{!!}}-k\cdot lg(f_{R^{!!}}\cdot[R^{!!}])\right)(13)$$

Equation (10) is logarithmic and determined $lg\,a_{R^!_nO_m}$and$lg\,a_{R^{!!}_kO_p}$

$$lg\,a_{R^!_nO_m}=-\frac{1}{x}\cdot\left(lg\,K_{R^!R^{!!}}+y\cdot lg\,a_{R^{!!}_kO_p}\right)\qquad(14)$$

$$lg\,a_{R^{!!}_kO_p}==-\frac{1}{y}\cdot\left(lg\,K_{R^!R^{!!}}+x\cdot lg\,a_{R^!_nO_m}\right)\qquad(15)$$

To find the dependence of the activities of oxides $R^{!!}_kO_p$and $R^!_nO_m$on the concentrations of deoxidizing elements, equations (14) and (15), respectively, are substituted into equation (13).

$$lg\,a_{R^{!!}_kO_p}=\frac{pmx}{mx+py}\cdot\left(\frac{1}{p}lg\,K_{R^{!!}}+\frac{k}{p}lg(f_{R^{!!}}\cdot[R^{!!}])-\frac{1}{mx}lg\,K_{R^!R^{!!}}-\frac{1}{m}lg\,K_{R^!}-\frac{n}{m}lg(f_{R^!}\cdot[R^!])\right)\qquad(16)$$

$$lg\,a_{R^!_nO_m}=\frac{mpy}{mx+py}\cdot\left(\frac{1}{m}lg\,K_{R^!}+\frac{n}{m}lg(f_{R^!}\cdot[R^!])-\frac{1}{py}lg\,K_{R^!R^{!!}}-\frac{k}{p}lg(f_{R^{!!}}\cdot[R^{!!}])-\frac{1}{p}lg\,K_{R^{!!}}\right)\qquad(17)$$

Replacing the activities of the reaction products in equations (11) and (12) through expressions (16) and (17) makes it possible to calculate the oxygen concentration in steel in equilibrium with deoxidizing elements .

$$lg([O])_{R^!}=-\frac{x}{py+mx}lg\,K_{R^!}-\frac{xn}{py+mx}lg(f_{R^!}\cdot[R^!])-\frac{1}{py+mx}K_{R^!R^{!!}}-\frac{yk}{py+mx}lg(f_{R^{!!}}\cdot[R^{!!}])-\frac{y}{py+mx}lg\,K_{R^{!!}}-lg\,f_O\qquad(18)$$

$$lg([O])_{R^{!!}}=-\frac{y}{py+mx}lg\,K_{R^{!!}}-\frac{yk}{py+mx}lg(f_{R^{!!}}\cdot[R^{!!}])-\frac{1}{py+mx}K_{R^!R^{!!}}-\frac{x}{py+mx}lg\,K_{R^!}-\frac{xn}{py+mx}lg(f_{R^!}\cdot[R^!])-lg\,f_O\qquad(19)$$

$$lg([O])_{R^!R^{!!}}=-\frac{1}{py+mx}K_{R^!R^{!!}}-\frac{x}{py+mx}lg\,K_{R^!}-\frac{y}{py+mx}lg\,K_{R^{!!}}-\frac{xn}{py+mx}lg(f_{R^!}\cdot[R^!])-\frac{yk}{py+mx}lg(f_{R^{!!}}\cdot[R^{!!}])-lg\,f_O\qquad(20)$$

In the joint deoxidation of steel with any alkaline earth metal (ACH), aluminum and silicon, the formation of complex complex aluminates, silicates and aluminosilicates is possible. Very stable compounds are silicates and barium aluminates. When multicomponent alloys are used, the formation of complex low-melting oxide and oxysulfide compounds and eutectics is possible. In this case, the most important component of these alloys is barium, which makes it possible to obtain very low-melting deoxidation products.

For preliminary deoxidation and alloying of various steels, as a rule, ferrosilicon grades FS45 and FS65 are used, containing up to 2.5% wt. aluminum or ferrosicoaluminum FS45A15. Therefore, the issue of the formation of complex compounds of the type $xAl_2O_3 \cdot ySiO_2$in the production of steel 20GL is very important.

Two options for the joint deoxidation of steel by silicon and aluminum are considered: the formation of both mullite $3Al_2O_3 \cdot 2SiO_2$and kyanite $Al_2O_3 \cdot SiO_2$[2]. The decomposition reactions of these compounds, as well as the equilibrium constants for these reactions, are presented below.

$$3Al_2O_3 + 2SiO_2 = 3Al_2O_3 \cdot 2SiO_2, \text{ where } K_{3Al_2O_3 \cdot 2SiO_2} = \frac{a_{3Al_2O_3 \cdot 2SiO_2}}{a^3_{Al_2O_3} \cdot a^2_{SiO_2}} \quad (21)$$

$$Al_2O_3 + SiO_2 = Al_2O_3 \cdot SiO_2, \text{ where } K_{Al_2O_3 \cdot SiO_2} = \frac{a_{Al_2O_3 \cdot SiO_2}}{a_{Al_2O_3} \cdot a_{SiO_2}} \quad (22)$$

According to the work, the value $lg\,K_{3Al_2O_3 \cdot 2SiO_2}$at a temperature of 1873 K is taken equal to 1.2 and we accept the expression $lg\,K_{Al_2O_3 \cdot SiO_2} = 8765/T - 0{,}63$, at 1873 K. $lg\,K_{Al_2O_3 \cdot SiO_2} = 4{,}05$[6]According to the recommended thermodynamic data [5], we accept the expression at 1873 K $lg\,K_{Al_2O_3} = 13{,}7742$ и $lg\,K_{SiO_2} = 4{,}6482$.Assuming that the resulting complex oxides $3Al_2O_3 \cdot 2SiO_2$and $Al_2O_3 \cdot SiO_2$are the only products of the corresponding deoxidation reactions, then their respective activities $a_{3Al_2O_3 \cdot 2SiO_2}$and $a_{Al_2O_3 \cdot SiO_2}$are taken equal to unity, and equations (21) and (22) take the form.

$$K_{3Al_2O_3 \cdot 2SiO_2} = \frac{a_{3Al_2O_3 \cdot 2SiO_2}}{a^3_{Al_2O_3} \cdot a^2_{SiO_2}} = \frac{1}{a^3_{Al_2O_3} \cdot a^2_{SiO_2}} = 1{,}2 \quad (23)$$

$$K_{Al_2O_3 \cdot SiO_2} = \frac{a_{Al_2O_3 \cdot SiO_2}}{a_{Al_2O_3} \cdot a_{SiO_2}} = \frac{1}{a_{Al_2O_3} \cdot a_{SiO_2}} = 4{,}05 \quad (24)$$

$$2 \cdot [Al] + 3 \cdot [O] = Al_2O_3, \text{ where } K_{Al_2O_3} = \frac{a_{Al_2O_3}}{a^2_{Al} \cdot a^3_O} = \frac{a_{R^!_nO_m}}{f^2_{Al} \cdot [Al]^2 \cdot f^3_O \cdot [O]^3} \quad (25)$$

Using the data of equations (25), (21) and (23) for the reactions of formation of mullite $3Al_2O_3 \cdot 2SiO_2$; (16), (22) and (24) for kyanite $Al_2O_3 \cdot SiO_2$, equation (12) for calculating the oxygen concentration can be written, respectively, in the form

$$lg[O]_{3Al_2O_3 \cdot 2SiO_2} = -\frac{1}{13} lg\,K_{3Al_2O_3 \cdot 2SiO_2} - \frac{3}{13} lg\,K_{Al_2O_3} - \frac{2}{13} lg\,K_{SiO_2} - \frac{6}{13} lg(f_{Al} \cdot [Al]) - \frac{2}{13} lg(f_{Si} \cdot [Si]) - lg\,f_O \quad (26)$$

$$lg[O]_{Al_2O_3\cdot SiO_2} = -\frac{1}{5} lg\, K_{Al_2O_3\cdot SiO_2} - \frac{1}{5} lg\, K_{Al_2O_3} - \frac{1}{5} lg\, K_{SiO_2} - \frac{2}{5} lg(f_{Al}\cdot [Al]) - \frac{1}{5} lg(f_{Si}\cdot [Si]) - lg\, f_O \quad (27)$$

$$lg[O]_{Al_2O_3} = -\frac{1}{3} lg\, K_{Al_2O_3} - \frac{2}{3} lg(f_{Al}\cdot [Al]) - lg\, f_O \quad (28)$$

Component activity factor a- $f_a$calculated using the following formula.

$$lg\, f_a = [a]\cdot e_a^a + [b]\cdot e_a^b + [c]\cdot e_a^c + \dots \quad (29)$$

where a, b, are the components in the alloy.

$e_i^j$is the first-order interaction parameter.

The oxygen concentration in the calculations is determined from equation (28) for a strong deoxidizer , taking the activity of the reaction product and the activity coefficients of oxygen and the deoxidizer equal to unity.

$$lg[O] = \frac{1}{m}(-lgK_{R'} - nlg[R']) \quad (30)$$

In a pair of aluminum , silicon, aluminum is a stronger deoxidizer , so the oxygen concentration for aluminum is calculated from the expression for the equilibrium constant of reaction (25) using equation (30).

$$lg[O] = \frac{1}{3}(-13{,}7742 - 2lg[Al]) \quad (31)$$

Table 12 - First order interaction parameters e_i^jin iron at 1873 K [6-13]

j \ i	C	Mn	Si	Al	S	P	Cr	Ca	Ba	O
C	0.243	-0.0084	0.08	0.043	0.044	0.051	-0.024	-0.097	n.a.	-0.32
Mn	-0.0538	0	-0.0327	-0.031	-0.048	-0.06	0	0.0004	n.a.	-0.083
Si	0 , 18	-0.0146	0.103	0.058	0.066	0.09	-0.0003	-0.066	n.a.	-0.119
Al	0.091	-0.013	0.056	0.043	0.035	0.033	0	-0.047	n.a.	-1.98
Cr	-0.12	0	-0.0043	0	-0.02	-0.053	-0.0003	0	n.a.	-0.14
Ca	-0.34	0.0015	-0.096	-0.072	-0.283	-0.215	0	-0.002	n.a.	-580
Ba	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	-445
O	- 0.421	-0.021	0.066	-1.17	-0.133	0.07	-0.04	-515	-52	-0.17

Let us determine, according to the formula (45), the activity coefficient of aluminum

$$lg\, f_{Al} = 0{,}043\cdot [Al] + 0{,}091\cdot 0{,}22 - 0{,}013\cdot 1{,}25 + 0{,}056\cdot [Si] + 0{,}033\cdot 0{,}025 + 0{,}035\cdot 0{,}02 - 1{,}98\cdot [O] = 0{,}043\cdot [Al] + 0{,}056\cdot [Si] - 0{,}0053 - 1{,}98\cdot [O] \quad (32)$$

Determine the activity coefficient of silicon

$$lg\, f_{Si} = 0{,}058\cdot [Al] + 0{,}18\cdot 0{,}22 - 0{,}0146\cdot 1{,}25 + 0{,}103\cdot [Si] + 0{,}09\cdot 0{,}025 + 0{,}066\cdot 0{,}02 - 0{,}119\cdot [O] = 0{,}058\cdot [Al] + 0{,}103\cdot [Si] + 0{,}025 - 0{,}119\cdot [O] \quad (33)$$

Let's determine the coefficient of oxygen activity

$$lg\, f_O = -1{,}17\cdot [Al] - 0{,}421\cdot 0{,}22 - 0{,}021\cdot 1{,}25 + 0{,}066\cdot [Si] + 0{,}07\cdot 0{,}025 + 0{,}133\cdot 0{,}02 - 0{,}17\cdot [O] = -1{,}17\cdot [Al] + 0{,}066\cdot [Si] - 0{,}114 - 0{,}17\cdot [O] \quad (34)$$

Getting the equation (32), (33) and (34) we put on (26), and the place of the oxygen concentration of the left equation we put the equation (31), then we get the transformation series (35).

$$[O]_{3Al_2O_3\cdot 2SiO_2} = 10^{-\frac{1}{13}\cdot(50{,}0772-17{,}292\cdot[Al]+6\cdot lg[Al]+1{,}326\cdot[Si]+2\cdot lg[Si]-14{,}43\cdot 10^{\frac{1}{3}\cdot(-13{,}7742-2\,lg[Al])})}$$

(35)

Getting the equation (31), (32) and (33) we put on (27), and place the oxygen concentration of the left equation we put equation (30), then we get the transformation series (36).

$$[O]_{Al_2O_3\cdot SiO_2} = 10^{-\frac{1}{5}\cdot(21{,}9168-5{,}706\cdot[Al]+2\cdot lg[Al]-5{,}635\cdot[Si]+2\cdot lg[Si]-2{,}949\cdot 10^{\frac{1}{3}\cdot(-13{,}7742-2\,lg[Al])})}$$

(36)

We supply the equation (32) and (34) to (28), and place the oxygen concentration of the left equation in equation (30), then we obtain the transformation series (37).

$$lg[O]_{Al_2O_3} = 10^{-\frac{1}{3}\cdot(13{,}4216-3{,}424\cdot[Al]+2\cdot lg[Al]+0{,}31[Si]-4{,}47\cdot 10^{\frac{1}{3}\cdot(-13{,}7742-2\,lg[Al])})} \quad (37)$$

Equations (35), (36), and (37) were used to calculate the equilibrium oxygen concentration in the case of joint deoxidation of 20GL steel melts by aluminum and silicon.

The results of calculations of the oxygen solubility in a melt of 20GL steel composition at 1873 K during complex deoxidation with aluminum and silicon are shown in the form of a graph (Fig. 1).

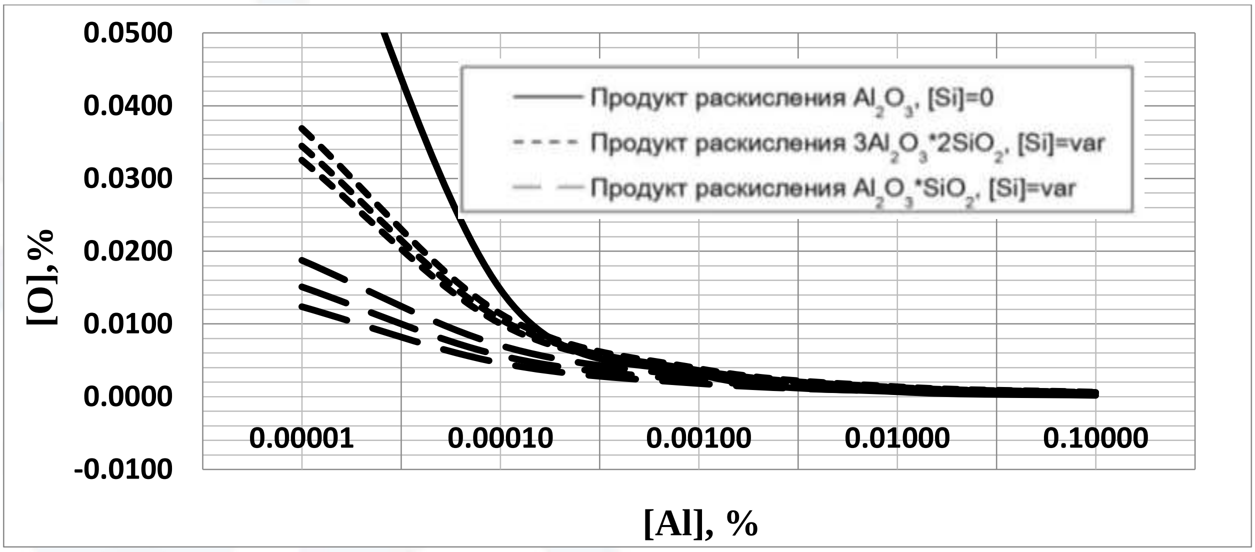

Figure 1 - Dependences of the solubility of oxygen in the melt composition of steel 20GL at a temperature of 1873 K on the concentration of silicon and aluminum

3.Conclusions

The carried out thermodynamic calculations of deoxidation processes showed the possibility of achieving low oxygen concentrations in 20GL steel, down to a level of less than 20 ppm at significantly lower aluminum concentrations (0.0010), which ensures a high level of steel purity for non-metallic inclusions when using combined deoxidation with aluminum and silicon. At a temperature of 1600 0C, the reaction products of ferrosilicoaluminum are in a liquid state and, therefore, are better removed into the slag.

In the case of complex deoxidation of steel with aluminum and silicon, the oxygen content and oxygen activity are lower than in the case of deoxidation with aluminum alone.

Based on the results obtained, it can be concluded that this calculation scheme can be the basis for calculating the oxygen solubility for 20GL grade steels in the variant of complex deoxidation with two deoxidizer elements.

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