

Deoxidizing capacity of aluminum in liquid iron. Literary source review

Nazyuta L. Yu.

*Doctor of Engineering, Professor
Azov State Technical University
Mariupol, Ukraine
E-mail: nazuta_l_u@pstu.edu*

Denisenko V. S.

*Postgraduate,
Azov State Technical University
Mariupol, Ukraine*

Abstract

The mechanism of iron deoxidation with aluminum in the formation of spinel ($\text{Fe} \cdot \text{Al}_2\text{O}_4$ – hercynite) or alumina (Al_2O_3 – α -corundum) was analyzed in the work on the basis of published data of the theoretical and experimental studies of various authors. The areas of co-existence and the deoxidation constant under the temperatures of steelmaking processes are determined.

It is shown that the results of thermodynamic analysis of the iron deoxidation reaction with aluminum and the content of aluminum $[\text{Al}] = 0.01 \div 0.0001\%$ correspond well with the experimental data of many authors and, therefore, they can be used for estimating its deoxidizing capacity. At higher aluminum content there is a significant dispersion in estimates of the equilibrium oxygen content. This is due to a change in the melt structure and the aluminum influence on the activity coefficient of oxygen (through the interaction parameter e_o^{Al}).

The main reason for discrepancy between theoretical and experimental data is the lack of reliable calculation method of the interaction parameters which takes into account the influence of composition on the activity of oxygen in the system. If deoxidation product is alumina, according to various sources at the temperature of 1600 °C $e_o^{\text{Al}} = -(1,0 - 8,3)$, and deoxidation constant is $K_{\text{Al-O}}^{-1} = 3 \cdot 10^{-9} - 4,5 \cdot 10^{-14}$.

According to the analysis the most probable values of these parameters are $e_o^{\text{Al}} = -(1,0-1,17)$, and $K_{\text{Al-O}}^{-1} = 1,6 - 2,4 \cdot 10^{-14}$

Key words: DEOXIDATION, EQUILIBRIUM, DEGREE OF OXIDATION, DEOXIDATION CONSTANT, INTERACTION COEFFICIENTS, MODIFICATION, NON-METALLIC INCLUSIONS, ALUMINA, SPINEL

Work objective is a comparison of the values of deoxidizing capacity of aluminum obtained by different authors on the basis of thermodynamic analysis and experimental data using various techniques. Selection of the most reliable values of the constants of the iron deoxidation with aluminum. Checking the effectiveness of Wagner's theory is used to estimate the thermodynamic activity of aluminum and oxygen dissolved in the iron.

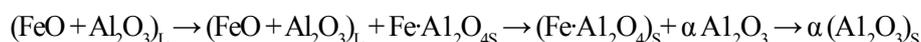
Aluminum is the one of the main steel deoxidizers. However, in many grades of steel smelting aluminum is used as an alloying element [1 - 5].

For example, in the low-carbon structural steel 08U the main deoxidizer is aluminum. Latter expended on deoxidation and alloying of the melt. In the process of crystallization part of the soluble aluminum is consumed in the formation of aluminum nitride, which neutralizes the effect of aging. This steel contains 0.04-0.09% of aluminum the basic amount of which is in a free state, and the amount of fixed aluminum (consisting of oxides and nitrides) is from 15% to 40% [6]. To provide the required content of free aluminum in the steel, it is added in several steps.

The transformer sheet contains 0.2-0.4% of the total aluminum. The proportion of fixed aluminum is less than 30% and it significantly affects the magnetic properties of the metal.

The quality of steel is determined on the one hand by the content of free aluminum (acid soluble) protecting it from secondary oxidation. On the other hand, it is determined by the amount and phase composition (morphology) of the non-metallic inclusions and forming nitrides and carbides of the aluminum. With the increase of nitrides the steel strength properties are grown. The initial temperature of nitride formation for the most grades of steel is 1200 - 1225 °C [7].

These factors should be considered when design-



When the temperature is 1700 °C according to these authors, there is no stable mutual solubility in the solid phases $\text{FeO} \cdot \text{Al}_2\text{O}_3$ and Al_2O_3 . According to

M. Ya. Medzhybozhskiy [3] when a residual aluminum content in the metal is (0.001-0.01%), which are commonly found in practice, the deoxidation products are presented with solid alumina or oxide phase, concentrated with alumina.

In this regard, the analysis of aluminum deoxidizing capacities and the composition of non-metallic inclusions formed during deoxidation and metal crystallization is of the scientific and practical interest.

Questions of studying a deoxidizing capacity of

ing the optimal deoxidation technology of many steel grades, especially for superduty steels, which include low-carbon, low silicate rail and pipe steels.

Aluminum is the stronger deoxidizer than silicon and manganese.

When adding the aluminum in the iron which contains oxygen, according to the diagram $\text{FeO} - \text{Al}_2\text{O}_3$ either pure alumina (with high content of Al_2O_3), or spinel $\text{FeO} \cdot \text{Al}_2\text{O}_3$ ($\text{Fe} \cdot \text{Al}_2\text{O}_4$ – hercynite) can be formed. The melting point of the pure alumina is about 2050 °C. The spinel melting temperature is 1800°C (1825 ± 15 °C [8]). This is significantly higher than the temperature of liquid bath.

The spinel is formed at relatively low aluminum content in the liquid iron (less than 0.001% [3]). As its increasing the deoxidation products content is changed. They are concentrated with alumina and equilibrium condition is characterized by the coexistence of beneficiated with alumina liquid $\text{FeO} \cdot \text{Al}_2\text{O}_3$ - phase and solid alumina. The content of alumina in the deoxidation products depends on the ratio of aluminum and oxygen concentration in the melt. The higher is the aluminum content, the lower is the proportion of spinel.

At higher concentrations of aluminum, only Al_2O_3 can exist in equilibrium with the metal. When the ratio of the concentration is $[\text{Al}] / [\text{O}] > 25$ only the inclusion of alumina (α - corundum) are detected [9].

In the process of crystallization the aluminum deoxidizing capacity increases. Therefore solid alumina is always present in the steel. The purity of the metal with these non-metallic inclusions is the main sign of the steel quality.

According to I. A. Novokhatskiy and B. F. Popov [8] within the temperature range 1535-1750 °C the equilibrium deoxidation products of iron with aluminum with increasing of the aluminum content changed as follows:

such a strong deoxidizer as aluminum attract special attention of scientists of all countries. However, due to the high deoxidizing capacity of aluminum when studying equilibrium processes, there is a number of difficulties associated with the low equilibrium concentrations of the elements and oxygen potential of gas phase, which in some cases are less than the analysis errors.

The most famous works on the study of equilibrium in the system Fe-O-Al are shown in Table 1. The methods of investigation of the temperature influence on equilibrium constant $K_{\text{Al-O}}$, the spinel or alumina formation reaction, deoxidation value constant

(K_{Al-O}^{-1} – a reciprocal of the equilibrium constant) at a temperature of 1600 °C, as well as the interaction parameters e_O^{Al} and e_{Al}^{Al} are shown. The letter takes into account the influence of aluminum on the activity coefficients of oxygen and aluminum itself. The parameters of interaction according to the theory of Wagner for infinitely diluted solutions were defined as partial derivatives:

$$e_O^{Al} = \frac{d \lg f_O}{d[Al]} = \frac{\lg a_{[O]} - \lg [O]}{[Al]}, \quad (1)$$

$$e_{Al}^{Al} = \frac{d \lg f_{Al}}{d[Al]} = \frac{\lg a_{[Al]} - \lg [Al]}{[Al]}. \quad (2)$$

Considering the importance of iron deoxidation with aluminum which is the main deoxidizer of steel and is used in almost all the array of melting metal in our country and abroad, the amount of analyzed data is large enough and includes thermo-dynamic and practical research of the known scientists using different methods for determination of oxygen equilibrium concentration including equilibrium in a controlled atmosphere H_2O/H_2 and CO_2/CO and by EMF. The latter is considered the most promising for the study of deoxidation processes, and especially in workshop conditions.

The number of studies on the equilibrium with hercynite (in [5] the formation of spinel is allowed when aluminum content is less than 0.007%) is very limited. The experimental data of A. McLean and R. Ward [10] are the most commonly used, which recommend determining deoxidation constant by the equation:

$$\lg K^{-1}_{Al-O} = \lg [Al]^2 \cdot a_{[O]}^{-4} = -\frac{71730}{T} + 23,25 \quad (3)$$

According to calculations at the temperature of 1600 °C – $K^{-1}_{Al-O} = 9,01 \cdot 10^{-16}$, the temperature of 1530 °C – $K^{-1}_{Al-O} = 2,9 \cdot 10^{-17}$. The results of this equation are almost coincided with the thermo-dynamic calculations of I. S. Kulikov.

In order to predict the composition of non-metallic inclusions the content of aluminum is of practical importance, at which the system $FeO \cdot Al_2O_3 - Al_2O_3$ is in the equilibrium. The equilibrium point of the system, in which both phases are coexisted, can be determined by simultaneous solution of the equations for $FeO \cdot Al_2O_3$ and Al_2O_3 .

According to the calculations of I. S. Kulikov this value is significantly less than the actual concentration of aluminum in the metal and at $T = 1600$ °C it will be $[Al] = 4,8 \cdot 10^{-4} \%$.

The concentration of aluminum in the metal at which saturated alumina deoxidation products are

formed S. Levin recommends to determine by the equation [12]:

$$[\%Al] = \sqrt[3]{1/K_{Al-O} (\%FeO)_{sat}} \quad (4)$$

where $(\%FeO)_{sat}$ – FeO content in the saturated deoxidation products which can be determined from the equilibrium diagram of the system.

The temperature effect on the equilibrium content of aluminum and oxygen during saturation of the deoxidation products with alumina has been calculated by the author using experimental data of A. N. Morozov and A. I. Strogonov [22], is represented in Table 1.

Table 1. The equilibrium content of aluminum and oxygen in the metal when saturating deoxidation products with alumina

Temperature, °C	Concentration, %	
	[Al]	[O]
1530	$0.8 \cdot 10^{-4}$	0.015
1600	$1.2 \cdot 10^{-4}$	0.025
1650	$1.6 \cdot 10^{-4}$	0.034

As follows from the data at $T = 1600$ °C the equilibrium in the system

$FeO \cdot Al_2O_3 - Al_2O_3$ occurs when the content of $[Al] = 1,2 \cdot 10^{-4} \%$. $[O] = 0.025 \%$ will be at the equilibrium with it. In the process of crystallization with decreasing the temperature deoxidizing capacity of aluminum is almost twice increased. At $T = 1530$ °C the equilibrium oxygen content will be $[O] = 0.015 \%$.

As the main product of the iron deoxidation by aluminum almost all authors consider Al_2O_3 . When analyzing the presented in the Table 1 data of the aluminum deoxidation during the formation of alumina the significant range of the constants values obtained experimentally (by 2-5 orders) draws special attention.

The first attempts to determine deoxidizing capacity of aluminum were based on thermodynamic calculations of the equilibrium constant. D. Chipman and D. Elliot [36] obtained at a temperature of 1600° C the following constant value of iron deoxidation aluminum $K^{-1}_{Al-O} = [Al]^2 \cdot [O]^3 = 1 \cdot 10^{-14}$ with taking into account the deviation of the oxygen and aluminum solution in the liquid iron from the ideal.

Thermo-dynamic calculations of other authors confirmed the order of this magnitude. According to I. S. Kulikov at the given temperature the deoxidation constant is $K^{-1}_{Al-O} = 3.3 \cdot 10^{-14}$, in the work of Z. Buzhek and A. Hutla

$K^{-1}_{Al-O} = 1.72 \cdot 10^{-14}$, according to Fruehan data K

$$K_{Al-O}^{-1} = 4.5 \cdot 10^{-14}$$

Then at a temperature of 1600 °C in equilibrium with 0.01% of aluminum

4,6-7,7·10⁻⁴ % of the oxygen will be located. It should be noted that at industrial experiment conditions the actual oxygen content is 0.002-0.006%. It is considerably higher than that calculated from the equilibrium condition and it almost does not depend on the concentration of the dissolved aluminum.

The lowest deoxidizing capacity of aluminum is obtained in experimental works of I. A. Novokhatskiy and B. F. Belov [8] when studying the metal-slag equilibrium ($K_{Al-O}^{-1} = 8 \cdot 10^{-9}$), and also at works of Hilty and Crafts when adding the aluminum to the iron melt by the method of rotating disc ($K_{Al-O}^{-1} = 3 \cdot 10^{-9}$). According to these authors at $T = 1600$ °C in equilibrium with 0.01 % Al, the 3.1-4.3·10⁻² of oxygen will be located.

Some scientists doubt the reliability of the results. According to G. M. Itskovich the low deoxidizing capacity of aluminum may be due to oxidation of the iron and the lack of the experiment accuracy.

However, the data of these authors are well corresponded with the thermo-dynamic calculations and experimental data of L. P. Vladimirov and L. M. Kopitsa (the EMF method) and with the results of H. Schenk in the study of the

Al₂O₃ dissolution process in the iron melt. In these studies the deoxidation constant is respectively 7-8·10⁻¹⁰.

In experimental works of V. I. Yavorskiy [35] using the method of EMF deoxidation constant is $K_{Al-O}^{-1} = 5.6 \cdot 10^{-11}$, that is three orders more than constants calculated by the thermo-dynamic data.

The most reliable are the data obtained by N. Gokken and D. Chipman [17] during the experiments in a controlled atmosphere (equilibrium is H₂O/H₂). At the temperature of 1600 °C the value of deoxidization constant is $K_{Al-O}^{-1} = a_{Al}^{-2} \cdot a_0^3 = 2,04 \cdot 10^{-14}$. In this paper we take into account the deviation of solution from the ideal with the help of interaction parameters. The data of these authors may be used at relatively high aluminum content and /or the presence of alloying elements in the metal. They are most often used in the foreign and domestic literature to determine the deoxidizing capacity of aluminum. For example, in the work [37] the comparison of the actual values of deoxidization constants of iron with aluminum with equilibrium values of this magnitude has allowed to determine the system deviation degree from the equilibrium and the size of critical nucleus of Al₂O₃.

The isotherms of iron deoxidation with aluminum according to various authors at the temperature of

1600 °C are shown in Fig. 1. As can be seen from the data, when the content of aluminum is $[Al] = 0,01 \div 0,0001\%$ the thermodynamic calculations are almost coincided with the experimental data of N. Gokken, D. Chipman and R. Fruehan using the different methods of researches.

By combining the results of different studies to determine the deoxidation constants Chino and Wada brought out the ratio [4], which is recommended by the Japanese Physical and Technical Committee to determine the deoxidizing capacity of aluminum:

$$\lg K_{Al-O}^{-1} = \lg a_{[Al]}^2 \cdot a_{[O]}^3 = -\frac{64900}{T} + 20,63 \quad (5)$$

The calculations based on this equation, when the content of aluminum is less than 0.01% may also be used in the metallurgical practice for estimating the equilibrium oxygen concentration.

At higher aluminum concentrations the significant differences in the estimates of the equilibrium oxygen content are observed. Thus, the higher is the aluminum content, the greater is the deviation of the experimental data by calculation. It is considered that this is due to changes in the structure of the melt, including the mutual influence of the components in the melt. According to I. A. Novokhatskiy and B. F. Belov this system should be considered from the perspective of regular ionic solutions with the mixing energy $Q = -11.66$ kJ/mol. The influence of aluminum on the activity coefficients of oxygen and aluminum tend to consider via the interaction parameters e_O^{Al} and e_{Al}^{Al} . At low concentrations of aluminum in the metal the value e_{Al}^{Al} is small; therefore, it is usually neglected.

Aluminum is the strong deoxidizer. The equilibrium concentration of oxygen in the metal deoxidized by aluminum at 1600 °C and the content of $[Al] = 0.01\%$ according to the different sources is not more than 1·10⁻³%. By increasing the concentration of aluminum in the metal this value should be reduced. However, the results of numerous experimental data for aluminum have a minimum of oxygen solubility $[O]_{min}$, after which the equilibrium oxygen content increases.

It should be noted that from the experimental data of various researchers

$[\% Al]_{extr.}$ varies widely in the range of 0.035-0.250, and the value of the parameter also varies e_O^{Al} from -1.45 to -8.3 units. Some foreign authors explain the discrepancy between experimental and calculated data that deoxidation products include not only pure alumina, but spinel FeO·Al₂O₃. Others believe that the main reasons for the large discrepancies are analytical errors in the determination of very low oxygen content, and the presence of the metal oxide inclu-

sions undeleted (aluminous suspensions), which in equilibrium is very difficult to remove from the metal. Others believe that the main reasons for the big discrepancies are analytical errors in determination of very low oxygen content and the presence of the unremoved metal oxide inclusions (aluminous suspensions), which in equilibrium are very difficult to remove from the metal. This is according to data of O.Repetilo, M. Olett and R. Kazakevich [38], which when carrying out the experiments under the argon atmosphere and oxidizing gas obtained the results differing by four orders of magnitude. The letter is explained by secondary oxidation of iron during the experiments with oxidized gas.

In the work of A. McLean and G. Bell using vapor-hydrogen mixture to the values of the interaction parameters at $T = 1600\text{ }^{\circ}\text{C}$ are $e_{\text{O}}^{\text{Al}} = -4.6$; and $e_{\text{Al}}^{\text{O}} = -7.8$. In the work of Gokken and Chipman [17] the interaction parameters values are much higher. They are $e_{\text{O}}^{\text{Al}} = -12$; and $e_{\text{Al}}^{\text{O}} = -20$.

In [23] when studying the process of the electrolytic iron deoxidation with aluminum in the induction furnace and under the argon atmosphere, the following values of the equilibrium constants and the interaction parameters (values in brackets are obtained by the extrapolation) are determined. They are shown in Table. 2.

Table 2. The effect of temperature on the value of deoxidation constants and interaction parameters

Temperature, $^{\circ}\text{C}$	1600	1760	1866
$\lg K_{\text{Al}}$	–	-711.2	-9.75
e_{O}^{Al}	(-1)	-0.92	-0.76
e_{Al}^{O}	0.048	(0.044)	(0.041)

The results of this work are well corresponded with the data of other researchers [16, 27, 30, 31]. Therefore, with high probability at temperature of 1600°C the values of the interaction parameters are $e_{\text{O}}^{\text{Al}} = -(1,0-1,17)$; and $e_{\text{Al}}^{\text{O}} = -(0,043-0,048)$. The last values do not significantly affect activity of aluminum, therefore, in the calculations we can use $a_{[\text{Al}]} = [\text{Al}]$.

By analyzing the experimental data of different authors I. S. Kulikov uses the value of the parameter $e_{\text{O}}^{\text{Al}} = -1.17$ for calculations at the temperature of $1600\text{ }^{\circ}\text{C}$, where $[\text{Al}]_{\text{extr.}} = 0.248\%$, and the minimum equilibrium oxygen content is $[\text{O}] = 3,1 \cdot 10^{-4}\%$. According to calculations of M. Ya. Medzhybozhskiy the aluminum content at the point of extremum is $[\text{Al}]_{\text{extr.}} = 0.12\%$, and the equilibrium concentration of oxygen –

$1.35 \cdot 10^{-40}\%$.

The influence of aluminum concentration on oxygen activity is well illustrated in represented in the figure isotherms of iron deoxidation by aluminum at $1550, 1600$ and $1650\text{ }^{\circ}\text{C}$ calculated by G. Knuppel according to the equation of Chin and Wada. As can be seen from the above data, when the aluminum content is more than 0.03% as a result of gradual changes in the structure of the melt the oxygen activity becomes smaller its concentration, and when $[\text{Al}] = 0.3\%$ the oxygen content reaches a minimum; further increasing of the aluminum concentration leads to a rapid increase of the oxygen concentrations, although the oxygen activity continues to decrease. This is a consequence of the aluminum influence on the activity coefficient of oxygen.

In the process of crystallization the aluminum deoxidizing capacity increases, and the amount of non-metallic inclusions decreases. According to [6] auto sheet steel 08U deoxidized by aluminum, the size of non-metallic inclusions selected after a secondary refining in the tundish is no more than 5.5 microns. When the crystallization temperature is $1530\text{ }^{\circ}\text{C}$ with 0.01% of aluminum there is $0.00013-0.00025\%$ of oxygen in equilibrium.

It should be noted that during the industrial experiment the actual oxygen content is $0.002-0.006\%$. It is considerably higher than that calculated by the equilibrium conditions and does not depend on the concentration of dissolved aluminum. According to D. Knuppel it is the evidence of commensurability of chemical reaction and removing non-metallic inclusions rates during the crystallization (no intensive stirring of the melt).

The composition of non-metallic inclusions formed during the oxidation of aluminum in actual conditions is of interest. It is believed that the formation of alumina happens only when there is an excess of aluminum content in the reaction zone. When the excess of oxygen is present the hercynite and variable content melt $m\text{FeO} \cdot n\text{Al}_2\text{O}_3$ are formed.

It should be noted that deoxidation of the molten metal with aluminum, a number of problems associated with a relatively low melting point and high thermal conductivity of aluminum appear. Aluminum is in the liquid state at steelmaking process temperatures, which requires special conditions of its introduction into the metal and influence the composition of deoxidation products. In connection with this in the process of deoxidation by aluminum there possible some changes of the interaction mechanism - in certain areas of metal the process may be limited by inside (deoxidizer supply) and/or outside (oxygen

supply) diffusion. In the first case, the formation of spinel is possible, in the second the pure alumina could be created. As the result the laminated non-metallic inclusions are formed. They contain in the center the spinel and the aluminous shell [19].

However, the laboratory studies of the nonmetallic inclusions composition formed during deoxidation of the electrolytic iron with ferroaluminum have confirmed the possibility of the formation at 1600 °C of complex inclusions in the center of which finely-devided particles of corundum are located. The shell was composed of particles of variable composition $m\text{FeO} \cdot n\text{Al}_2\text{O}_3$ [37]. Besides, aluminum introduced in excess due to high deoxidizing capacity can communicate not only with oxygen dissolved in the metal, but also with the oxides of weaker deoxidizers (MnO , SiO_2) forming more complex non-metallic inclusions. The morphology of non-metallic inclusions has a significant impact on the quality characteristics of the metal and, especially, when melting the low-carbon steel grades.

The main advantage of aluminum is its high deoxidizing capacity. However, in the process of deoxidation, usually rather large non-metallic inclusions based on alumina are formed. Thus the main task is to remove the alumina inclusions, which were formed during the initial stages of deoxidation before the metal crystallization is started. This problem is solved by pneumatic mixing of metal with inert gas, at the stage of secondary refining.

This is the great advantage of aluminum, since the addition of its small amount can completely bring steel at rest. Besides, the small value of the residual oxygen content to the start of steel casting, deoxidized with aluminum, the additional amount of inclusions formed during the crystallization of the metal and can be slightly modified by introducing the alkaline earth metals.

Conclusion

It is shown that the results of thermodynamic analysis of iron deoxidation reaction with aluminum where aluminum content is $[\text{Al}] = 0.01 \div 0.0001\%$ are well corresponded with the experimental data by many authors and therefore can be used to estimate its deoxidizing capacity. At higher aluminum content the considerable variation in the estimates of the equilibrium oxygen content is observed. This is due to the change in the structure of the melt and the influence of aluminum on the oxygen activity coefficient (through the interaction parameter e_o^{Al}).

The main reason for discrepancy between the theoretical and experimental data is the lack of reliable method of the interaction parameters calculation ta-

king into account the influence of the composition on the activity of oxygen in the system. If deoxidation product is alumina, according to the various sources at the temperature of 1600 °C $e_o^{\text{Al}} = -(1,0 - 8,3)$, and deoxidation constant $K_{\text{Al-O}}^{-1} = 3 \cdot 10^{-9} - 4,5 \cdot 10^{-14}$.

According to the analysis the most probable values of the interaction parameters are $e_o^{\text{Al}} = -(1,0-1,17)$, and $K_{\text{Al-O}}^{-1} = 1,6 - 2,4 \cdot 10^{-14}$

The study of the equilibrium existence of phases in Fe-O-Al system allows us to predict the composition of deoxidation products, and changes of oxygen activity in the iron at different temperatures and aluminum contents.

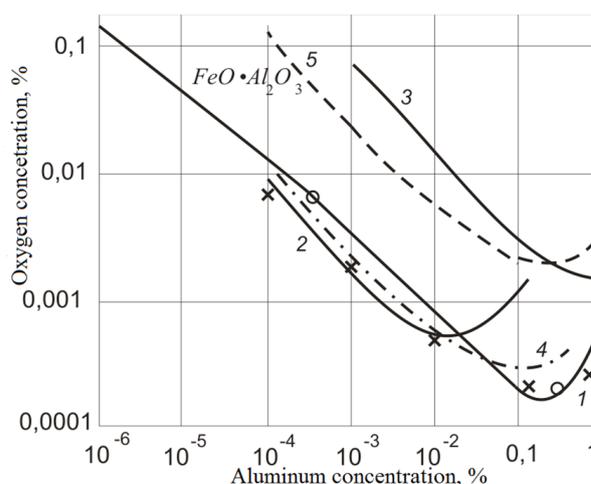


Figure 1. The isotherms of oxygen content in iron depending on the concentration of aluminum at 1600 °C: 1 - according to I. S. Kulikov [1], 2 - N. Gokken and D. Chipman [17], 3 - H. Schenk [26], 4 - R. Fruehan [14], 5 – L. P. Vladimirov and L. M. Kopitsa [16]

x - calculations according to the equation of Chino and Wada [4]

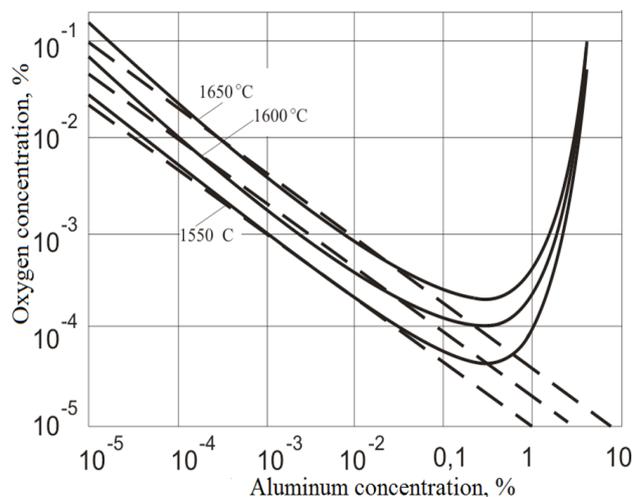


Figure 2. The isotherms of iron deoxidation with aluminum [4] Full lines - oxygen concentrations, the dotted lines - the oxygen activity

Table 3. Published data on the equilibrium reaction of iron deoxidation with aluminum

$\lg K_{Al-O}$	K_{Al-O}^{-1} (1600°C)	$e_O^{\#}$	$e_A^{\#}$	[Al], %	Method and references
Aluminum, reaction $Fe+2[Al]+4[O] \leftrightarrow FeAl_2O_4$					
72 22.948	180/T— $2.5 \cdot 10^{-16}$	-0.51	-	$<4.8 \cdot 10^{-4}$	Calculated according to thermodynamic data of I. S. Kulikov [1].
72 23.25	730/T— $9.01 \cdot 10^{-16}$	-	-	$<10^{-5}$	Metal equilibrium— $FeAl_2O_4$ A. McLean, R. Ward. [10]
59570/T-22.49	$4.84 \cdot 10^{-10}$	-	-	0 . 0 0 1 - 0.007	Metal slag equilibrium, I. A. Novokhatskiy, B. F. Belov [8]
Aluminum, reaction $2[Al]+3[O] \leftrightarrow Al_2O_3$					
63 20.586	790/T— $3,3 \cdot 10^{-14}$	-1.17	-	-	Calculated according to thermodynamic data of I. S. Kulikov [1].
64 20.56	290/T— $1.72 \cdot 10^{-14}$	-	-	-	Calculated according to thermodynamic data of Z. Buzhek A. Hutl [13]
62 20.17	780/T— $4.50 \cdot 10^{-14}$	-	-	-	Calculated according to R. Fruehan thermodynamic data [14]
64 20.41	090/T— $1.56 \cdot 10^{-14}$	-	-	-	Calculated according to thermodynamic data of A. McLean and R. Ward [20]
55 19.666	184/T— $1.6 \cdot 10^{-10}$	-	-	0.001 - 1	Calculated according to thermodynamic data L. P. Vladimirov and N. Kopitsa [16]
64 20.48	000/T— $2.04 \cdot 10^{-14}$	-12	-20	<0.1	Equilibrium H_2O/H_2 N.Gokken, D. Chipman [17]
45 11.55	500/T— $1.81 \cdot 10^{-13}$	-	-	-	Equilibrium H_2O/H_2 , crucibles from Al_2O_3 D. Swisher [15]
60 18.64	300/T— $2.54 \cdot 10^{-14}$	-4,6	-7,8	<1	Equilibrium H_2O/H_2 A. McLean, G. Bell [19]
58 18.9	600/T— $4.1 \cdot 10^{-13}$	-	-	-	Equilibrium CO_2/CO Geller and Dicke [18]
63 20.48	500/T— $3.78 \cdot 10^{-14}$	-	-	-	Equilibrium CO_2/CO Chipman and Langenberg [21]
68 22.85	601/T— $1.67 \cdot 10^{-14}$	-	-	-	Equilibrium CO_2/CO , crucibles from Al_2O_3 Niva [4]
	$1 \cdot 10^{-14}$	-1.0	-	<2	The addition of aluminum to the molten iron D. Entremont [23]
71 27.98	200/T— $9.2 \cdot 10^{-11}$	-	-	-	The addition of aluminum to the iron melt. Wentrup and Heber [24]
58 22.75	600/T— $3 \cdot 10^{-9}$	-	-	-	The addition of aluminum to the iron melt by rotating crucible method of Hilty and Crafts [25]

-		$6.99 \cdot 10^{-10}$	-0,22	-	10^{-3}	Dissolution of Al_2O_3 in the iron melt G. Schenk
64 20.57	000/T—	$2.51 \cdot 10^{-14}$	-1,17	-	<3	Equilibrium of the metal-lime-alumina slag L. Rode [27]
51 19.53	700/T—	$8 \cdot 10^{-9}$	-	-	-	Metal-slag equilibrium, I. A. Novokhatskiy, B. F. Belov [8]
-		$5.62 \cdot 10^{-14}$	-3.90	-	<0.4	EMF (electrolyte $ThO_2—Y_2O_3$) R. Fruehan [14]
62 20.54	680/T—	$1.19 \cdot 10^{-13}$	-	-	<2	<<Same>>(electrolyte $ThO_2—Y_2O_3$ A. Jacquem [29]
-		$2.41 \cdot 10^{-14}$	-1.0	-	0.0003-1.3	<<Same>> D. Yanke, W. Fischer [30]
39 11.05	284/T—	$1.19 \cdot 10^{-10}$	-0.943	-	0.001 - 1	<<Same>> L. P. Vladimirov and N. Kopice [16]
-		$5.6 \cdot 10^{-11}$	-	-	-	<<Same>> V. I. Yavoyskiy and et al. [35]
-		$3.20 \cdot 10^{-14}$	-1.15	-	<1.25	Processing of published data Z. Buzhek [32]
-		$1.50 \cdot 10^{-12}$	-	-	<0.3	Filtration of the iron-aluminum melts of D. Hupp., M. Fronberg [33]
64 20,63	900/T—	$1.04 \cdot 10^{-14}$	-	-	-	Processing of published data of Chino and Wada [4] Savamura [34]
64 20,57	306/T—	$1.56 \cdot 10^{-14}$	-0.96	-	0.077-1.64	K' as a function of [%Al], Z. Buzhek, A. Hutla [31]

References

1. Kulikov I. S. *Raskislenie metallov* [Deoxidation of metals], Moscow, Metallurgy, 1972, 207 p.
2. Itskovich G. M. *Raskislenie stali i modifitsirovanie nemetallicheskih vklyucheniy* [Deoxidation of steel and modifying of non-metallic inclusions], Moscow, Metallurgy, 1981, 296 p.
3. Medzhybozhskiy M. Ya. *Osnovyi termodinamiki i kinetiki staleplavilnyih protsessov* [The fundamentals of thermodynamics and kinetics of the steelmaking processes], Kiev, Donetsk: High school, 1979, 280 p.
4. Knuppel G. *Raskislenie i vakuumnaya obrabotka stali. Chast I. Termodinamicheskie i kineticheskie zakonomernosti* [Deoxidation and vacuum steel processing. Part 1: Thermodynamic and kinetic regularities], Moscow, Metallurgy, 1973, 312 p.
5. Yanke D. Literature review on the equilibrium of the most important deoxidizers elements with oxygen in the molten iron (1976), *Ferrous metals*, No.8, p.p. 26 - 30.
6. Luzgin V. P. Oxygen and steel quality (2002), *Steel*. No.6, p.p. 20 - 23.
7. Stomakhin A. Ya. Optimization of additives to steel of the nitride forming elements (2010), *Ferrous metals*,. No. 2, p.p. 15 - 19.
8. Novokhatskiy I. A. The phase equilibriums and distribution of the elements in the Fe-O-Al (1966), *Proceed. USSR Academy of Sciences, Metals*, No.1, p.p. 38-48.
9. Booker C.R. a. o. J. *Iron Steel Inst.*, 1960, v. 196, p.p. 294 – 300.
10. Mclean A.A. Ward R. G. J. *Iron Steel Inst.*, 1966, v. 204, p.p. 8—11
11. Luzgin V. P. Activity as a characteristic of interparticle interaction in equilibrium and non-equilibrium systems (1973), *Proceedings of the universities. Ferrous metallurgy*, No.9, p.p. 50 - 53.
12. Levin S. L. *Staleplavilnyie protsessy*[Steel-making processes], Kyiv, Technique, 1963, 434 p.
13. Buzek Z., Huta A. Freiberg. *Forsch., H., Rei-*

- he B, 1969, No.117, p.p. 59—73.
14. Fruehan R.J. Metallurg. Trans., 1970, 1, p.p. 3403—10.
 15. Swisher J.H. Trans. Metallurg. Soc. AIME, 1967, v. 239, p. p. 123-14.
 16. Vladimirov L. P., Kopice N. M. Theoretical and experimental determination of the deoxidizing capacity of aluminum with newest research methods (1971), *Universities Proceed. Ferrous Metallurgy*, No. 11, p.p. 18-22.
 17. Gokcen N. A., Chipman J. Trans, metallurg. Soc. AIME, 1953, 197, p.p. 173—78.
 18. Geller W. u. Dicke K. Arch. Eisenhüttenwesen, 1942/43, Bd 11/12, p.p. 431—36.
 19. McLean A., Bell H. B. J. Iron Steel Inst., 1965, 203, p.p. 123-30.
 20. Mclean A. Ward R. G. J., J. Metals, 1965, v. 17, p.p. 526-28.
 21. Chipman J., Langenberg F. – In.: “Physical Chemistry of Iron and Steelmaking”, N.Y., *Massachusetts Institute of Technology*, 1958, p. p. 45 – 70.
 22. Morozov A. N., Stroganov A. I. *Raskislenie martenovskoy stali* [Deoxidation of open-hearth steel] Moscow, Metallugizdat, 1955.
 23. Entremont J. C. de et al. Trans, metallurg. Soc. AIME, 1963, 227, p.p. 14—17.
 24. Wentrup H. a. Hieber G. Arch. Eisenhüttenwesen, 1939/40, Bd 1, p.p. 15—20.
 25. Hilty D.C.a. Graf ts W. J. Journal Metals, 1950,2, Trans, v. 188, p. 414-24, p. 1342-45.
 26. Schenck H. et al. Arch. Eisenhüttenwes., 1970, 41, p.p. 131-38.
 27. Rohde L. E. et al. Arch. Eisenhüttenwes., 1971, 42, p.p. 165-74.
 28. Povolotskiy D. Ya. The mechanism of non-metallic inclusions formation during deoxidation of iron (1969) , *Proceed. of USSR Academy of Sciences. Metals*, No. 4, p. p. 11-17.
 29. Jacquem o t A. et al. C. R. hebd. Seances Acad. Sci.^ Ser. C, Sci. chim., 1973, 277, p.p. 271-73.
 30. Yanke D., Fischer W. A. Arch. Eisenhüttenwes., 1976, 47, p. p. 147-51, 195-98.
 31. Buzek Z., Hutla A. Sbornik vedeckych praci' Vyso- ke Skoly banske v Ostrave, 1965, No.11, p. p. 375—78.
 32. Buzek Z. The effect of alloying elements on the solubility and activity o O and S in liquid Fe at 1600°. In: International symposium on metallurgical chemistry, 1971, VII, Univ. Sheffield.
 33. Hap p J., FrohbergM. G. GieP.-Forsch., 1971, 23, g j g,
 34. Sawamura H. – “Journal Iron and Steel Institutejapan”, 1964, v. 50, No.8, p. p. 1217 – 1220.
 35. Yavoysky V. I., Vladimirov L. P. , Luzgin V. P. The study of iron deoxidation thermodynamics by emf (1974) , *USSR Academy of Sciences Proceedings. Metals*, No. 2, p.p. 14-21.
 36. Chipman J., Elliott J. The production of steel in electric furnaces. Moscow, Metallurgy, 1965, p. p. 92 - 166.
 37. Repetylo O., Olette M., Kozakevitch , *Journal of Metals*, 1967. v. 19.No. 5, p. p. 45-49.
 38. Mchedlishvili V. A., Gongadze G. A., Samarin A. M. The study of the oxide nucleation process in liquid iron during the deoxidation with aluminum and silicon(1972), *USSR Academy of Sciences Proceedings. Metals*, No. 5, p.p. 10-19.

