

## Titanium deoxidation power in the liquid iron.

### Literary source review

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#### Abstract

This work provides an analysis of the mechanism of iron deoxidation with titanium based on the experimental and theoretical data. Depending on the titanium content in liquid melt Fe-Ti-O, the oxides are formed with different valences, which are of different crystal lattice structure: TiO (face-centered cube), TiO<sub>2</sub> (tetragonal lattice), Ti<sub>2</sub>O<sub>3</sub> (trigonal of  $\alpha$ -alumina type) and Ti<sub>3</sub>O<sub>5</sub> (orthorhombic). The thermodynamic characteristics of the basic process of deoxidation in the case of formation of each of these oxides, including deoxidation constant and interaction parameters at 1600 °C, was analyzed.

It is shown that the basic difficulties in determining of these parameters are associated with the identification of the reaction products, since the same content of titanium in the liquid melt, as well as the use of similar techniques provide the various oxides formation. Experimental data on the equilibrium constants  $K_{\text{TiO}_2}$ ,  $K_{\text{Ti}_3\text{O}_5}$ ,  $K_{\text{Ti}_2\text{O}_3}$  differ by almost 2 orders of magnitude. The authors try to adjust the inaccuracies in the deoxidation constant determination by the parameters of the interaction.

It should be noted that the data of different authors thermodynamic calculations of deoxidation constant for each oxide (regardless of the method of their calculation) differ slightly. At a temperature of 1600°C, their value according to different authors is relatively stable:  $K_{\text{TiO}_2}^{-1} = (5.1-7.0) \cdot 10^{-7}$ ,  $K_{\text{Ti}_3\text{O}_5}^{-1} = (4.1-4.6) \cdot 10^{-18}$ ;  $K_{\text{Ti}_2\text{O}_3}^{-1} = 2.7 \cdot 10^{-11}$ .

The studies by D. Yanke and B. Fisher using probes based on ThO<sub>2</sub> - Y<sub>2</sub>O<sub>3</sub> when measuring of oxygen activity are the most reliable. At a temperature of 1600°C, in the titanium content range of 0.001-0.1%, the value of the equilibrium constant is  $K_{\text{Ti}_3\text{O}_5} = 7.41 \cdot 10^{18}$  (the inverse value  $1.35 \cdot 10^{-19}$ ) according to their studies, and in the Ti content range of 0.1-3%, the value of the constant is significantly lower  $K_{\text{Ti}_2\text{O}_3} = 3.70^{11}$  (the inverse value  $2.70 \cdot 10^{-12}$ ).

The main reason for discrepancy between the theoretical and experimental data is the lack of a reliable method of the interaction parameters calculation that take into account the oxygen activity impact on the system. Interaction parameter  $e_{\text{Ti}}^{\text{Ti}}$ , which average value is 0.041, is relatively reliable.

Effect of titanium on the oxygen activity is ambiguous. If the titanium content is less than 0.2%, in the case of TiO<sub>2</sub> formation, an interaction parameter will be  $e_{\text{O}}^{\text{Ti}} = - (0.160 - 0.187)$ , in the case of Ti<sub>3</sub>O<sub>5</sub> formation,  $e_{\text{O}}^{\text{Ti}} = - (0.31 - 0.37)$ . If the concentration of titanium in the liquid melt is more than 0.2% (Ti<sub>2</sub>O<sub>3</sub> formation), its effect on the oxygen activity increases, the interaction parameter increases almost twice and is  $e_{\text{O}}^{\text{Ti}} = - (0.65 - 0.75)$ .

**Key words:** DEOXIDATION, EQUILIBRIUM, DEGREE OF OXIDATION, DEOXIDATION CONSTANT, INTERACTION PARAMETER, MODIFICATION, MICROALLOYING, NON-METALLIC INCLUSIONS

The work objective is comparison of titanium deoxidizing ability obtained by different authors on the basis of thermodynamic analysis and experimental data using various techniques; selection of the most reliable values of iron deoxidation with titanium constants in a wide range of titanium concentrations from  $10^{-4}$  to 1%.; check of the Wagner theory use effectiveness for the components thermodynamic parameters evaluation in the liquid melt Fe-Ti-O.

Titanium belongs to transition metals of IV A group of the periodic system (including zirconium, hafnium and thorium). Titanium order number is 22. The titanium density at a temperature of 20°C is 4.51 g/cm<sup>3</sup>. Melting point is 1667°C, and boiling point is 3179°C. In the chemical compounds, it exhibits a valence of 2, 3 and 4. The titanium outermost electron configuration is  $3d^24s^2$ .

Titanium has a high deoxidizing ability. However, titanium is preferably used for microalloying and steel modification in ferrous metallurgy. It is caused by the titanium carbides and nitrides specific properties; their melting point and strength are high. For example, the melting point of titanium nitride is 2950°C, and of titanium carbide is 3150°C. Titanium belongs to the strong ferrite-promoting elements. The titanium introduction contribute to the steel cold resistance increase, precipitation hardening due to fine-grain steel structure obtaining and non-metallic inclusions modification, including sulfides.

Titanium is found in many heat-resistant and stainless steels [1, 2]. The titanium content in heat-resistant steel is 0.2-0.4%. In the austenitic-ferritic stainless steel, titanium content is up to 0.8%. In some rust-resisting maraging steels, the titanium content can reach 2.8%. It is also used in the production of high-quality pipe steels. In the pipe steels 17G1SU, 17GS, and other, titanium content is 0.08-0.18%.

It is used in the production of low-carbon rust-resisting steels. It should be noted that the global trend of rust-resisting steels

metallurgy development, i.e. the carbon content of less than 0.03% reduction does not require expensive stabilizers (including titanium) in order to prevent the tendency to the grain-boundary corrosion. However, in the domestic markets of the CIS countries (including Russia and Ukraine), the titaniferous steels are the most demanded products. Titanium is used for binding of carbon and nitrogen in solid carbides and nitrides of titanium if there are no deep decarbonization conditions in the enterprises [3]. In these steels, the titanium content is 0.02 - 0.04%.

Analysis of iron deoxidation with titanium is one of the most difficult tasks. Titanium forms a series of oxides, which can form chemical compounds (e.g., FeO·TiO<sub>2</sub> - ilmenite) when interacting with iron oxides. It is explained by the structure features of outer shell of titanium atoms, which are capable to take the oxygen valence electrons into incomplete  $\alpha$ -electron shell under certain conditions when metallic bonding maintaining without the formation of ionic compounds or covalent linkage occurrence. At that, oxygen atoms of a small atomic radius are located in the titanium lattice forming interstitial phases. At higher oxygen content, the compounds with certain stoichiometric atoms arrangement are formed. Therefore, in the titanium-oxygen system, a large amount of oxide phases, including homologs Ti<sub>n</sub>O<sub>2n-1</sub> (when n=1-10), are formed. Usually in metallurgical processes, the oxides TiO (II), TiO<sub>2</sub> (IV), Ti<sub>2</sub>O<sub>3</sub> (III) and Ti<sub>3</sub>O<sub>5</sub> are analyzed. These oxides are of a higher melting point: TiO (1750°C), TiO<sub>2</sub> (1850°C), Ti<sub>2</sub>O<sub>3</sub> (2130°C) and Ti<sub>3</sub>O<sub>5</sub> (1830°C), as well as different crystal lattice structure: TiO (face-centered cube), TiO<sub>2</sub> (tetragonal lattice), Ti<sub>2</sub>O<sub>3</sub> (trigonal of  $\alpha$ -alumina type) and Ti<sub>3</sub>O<sub>5</sub> (orthorhombic).

Literary data on the resulting oxides composition are extremely contradictory. However, these data are necessary for the analysis of the titanium deoxidizing ability research results, since this element is

increasingly used during deoxidation for microalloying as part of complex deoxidizers. The equilibrium of reaction of iron melts deoxidation with titanium was investigated repeatedly. The greatest difficulties arise with the identification of deoxidation products. Since the same content of titanium in the liquid melt, as well as the use of similar techniques provide the various deoxidation products are found.

In B.K. Lyaudis' and A.M. Samarin's papers [4], the oxygen solubility in liquid iron containing titanium was studied in the induction furnace using steam- hydrogen mixture at temperatures 1600-1650°C. It was established that during iron deoxidation with titanium, the formation of liquid products  $2\text{FeO}\cdot\text{TiO}_2$  is possible in the area of titanium concentration of up to 0.04%, and the formation of solid particles  $\text{TiO}_2$  is possible at higher titanium concentrations of 0.04-0.5%. However, other authors' X-ray diffraction analysis of non-metallic inclusions have shown that a compound  $\text{Ti}_3\text{O}_5$  is the deoxidation product in this concentration range [5, 6].

According to G. Knyuppel', compounds of  $\text{FeO}\cdot\text{TiO}_2$  or  $\text{Ti}_3\text{O}_5$  (high temperature modification - anosovite) may be deoxidation products during iron deoxidation with titanium in the low titanium concentrations (less than 0.1%). If the titanium content in the iron is more than 0.1%, the oxides  $\text{TiO}_2$  or  $\text{Ti}_2\text{O}_3$  are formed. The analysis of thermodynamic parameters of reactions of fundamental titanium oxides  $\text{FeO}\cdot\text{TiO}_2$ ,  $\text{Ti}_3\text{O}_5$ ,  $\text{Ti}_2\text{O}_3$  and  $\text{TiO}$  formation carried out by I.S. Kulikov showed that at  $T=1600^\circ\text{C}$ , formation of  $\text{FeO}\cdot\text{TiO}_2$  is possible if the titanium content is up to  $1.1\cdot 10^{-4}\%$ .  $\text{Ti}_3\text{O}_5$  is formed if the titanium content is up to 0.3%. If the titanium content is 0.3-5%, the titanium oxide  $\text{Ti}_2\text{O}_3$  is the most stable, and a monoxide  $\text{TiO}$  may be in deoxidation products at higher contents [7].

As for titanium monoxide, which has a very wide range of homogeneity, the evaluation of its activities is quite difficult. According to thermodynamic analysis data, it must be formed if titanium content is more than 16%. However, according to E. Turkdogan's [8] and V.I. Yavoyskiy's [9] experimental data,  $\text{TiO}$  existence domain begins if a content is more than 5%.

It should be noted that the titanium dioxide  $\text{TiO}_2$  is usually not found in the titanium deoxidation products during iron

deoxidation with titanium. Obviously, this is related to the formation of complex chemical compounds, as when aluminum deoxidizing (it is approximately equal to the titanium deoxidizing capacity), or the presence of several deoxidation products in the non-metallic inclusions.

This is confirmed by the works carried out under the supervision of D.Ya. Povolotskiy [10], where on the basis of X-ray analysis of non-metallic inclusions, it is shown that formation of non-metallic inclusions various composition is possible during deoxidation process as a result of titanium concentration fluctuation. A great number of large globular inclusions of up to 100 microns of variable composition are found in the samples. The titanium content in the center of these inclusions is 40-65% which is significantly lower than at the periphery. According to the authors, these inclusions core contains significant amounts of iron oxide, and it is in a liquid state at steelmaking process temperature. Such inclusions were identified by the authors as a liquid, and therefore, they were removed easily from metal during secondary treatment.

In V.I. Yavoyskiy's paper [9], the X-ray patterns of non-metallic inclusions extracted by electrolysis from the metal samples were very weak and did not correspond to the structure of certain oxides in the system Fe-O-Al-Ti. In subsequent papers of these authors, by the method of X-ray structural analysis of slags, which were formed during the iron deoxidation with titanium, it was shown that their content depends upon the concentration of residual titanium in iron.  $\text{Ti}_3\text{O}_5$  (lattice type is anosovite) is formed if the titanium content is 0.08-0.18%,  $\text{Ti}_2\text{O}_3$  (lattice type is  $\alpha$ -alumina  $\text{Al}_2\text{O}_3$ ) is formed if the titanium content is up to 3.6%,  $\text{TiO}$  or  $\text{TiO}+\text{Ti}_2\text{O}_3$  (lattice type is NaCl) are formed if the titanium content is more than 5%.

In the G.A. Gongadze V.A. Mchedlishvili's paper [11], the composition of formed non-metallic inclusions was investigated in the argon medium during iron deoxidation with titanium at 1600°C. It was established that the deoxidation products are heterogeneous and consists of two layers: I is directly adjacent to the surface of the metal contact with deoxidizer, and II appears at a distance of 4 mm from the surface after a 6 minute exposure. According to X-ray analysis data, the first layer inclusions are shown in the

form of globular iron-titanium oxide particles (FeO-TiO<sub>2</sub>) and rounded particles Ti<sub>2</sub>O<sub>3</sub>. The second layer inclusions are dendrid-type particles TiO<sub>2</sub>( rutile). The average oxygen content in the area of the second layer was 0.035%. The critical nucleus radius was A 3.8°. Such nucleus can be formed by the association of eight particles of TiO<sub>2</sub>.

In Table 1, according to various authors, an analysis of literary sources on the equilibrium in the system Fe - Ti - O is shown. This data are obtained using different research techniques, including the e.m.f. method, which gives the most accurate results when analyzing of the oxygen activity for each of the possible mechanisms of titanium oxidation. We described the investigation methods; the temperature effect on the equilibrium constant  $K_{Ti-O}$  of various oxides formation reactions;

deoxidation constant values ( $K_{Ti-O}^{-1}$  is value inverse to the equilibrium constant) at a temperature of 1600°C; and also the parameters of  $e_O^{Ti}$  and  $e_{Ti}^{Ti}$  interaction. The last considers the titanium effect on the activity coefficients of oxygen and titanium. In accordance with Wagner theory for infinitely dilute solutions, the interaction parameters were defined as partial derivatives:

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

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

Analysis of the data given in Table shows that TiO<sub>2</sub> or Ti<sub>3</sub>O<sub>5</sub> may be oxide phases in equilibrium with the titaniferous liquid melt at low titanium content of about 0.001-0.2%. If the titanium content is more than 0.2% (at least up to 3%), Ti<sub>2</sub>O<sub>3</sub> is in equilibrium with titanium, according to most authors. The experimental data on the equilibrium of the system with high titanium content of more than 5% (except the paper [25]) are practically absent.

In some cases, experimental data on the equilibrium constants  $K_{TiO_2}$ ,  $K_{Ti_3O_5}$ ,  $K_{Ti_2O_3}$  differ almost by two orders of magnitude. For example, at a temperature of 1600°C and the titanium content of up to 0.2%, the deoxidation constant ranges  $K_{TiO_2}^{-1} = 1.0 \cdot 10^{-6} - 3.17 \cdot 10^{-7}$  in the case of TiO<sub>2</sub> formation, and the value of

this parameter is of the different order  $K_{Ti_3O_5}^{-1} = 8 \cdot 10^{-17} - 5 \cdot 10^{-20}$  in the case of Ti<sub>3</sub>O<sub>5</sub> formation. If the titanium content is more than 0.2%, Ti<sub>2</sub>O<sub>3</sub> is formed, and according to various authors, the deoxidation constant will be  $K_{Ti_2O_3}^{-1} = 1.25 \cdot 10^{-10} - 2.7 \cdot 10^{-12}$ . The authors try to adjust the inaccuracies in the deoxidation constant determination, including that, which are caused by research methods imperfection and the complexity of deoxidation product identification, by the parameters of the interaction.

The isothermal lines of iron deoxidation with titanium at 1600°C are presented in Figure 1. Here, I.S. Kulikov's isothermal line is depicted considering formation of various deoxidation products.

In the titanium concentration range of 0.001-0.1%, the highest deoxidizing ability of titanium is found in the works of German scientists (using of modern methods of analysis of the oxygen activity by e.m.f. method [25]) and of Tokyo Research Institute scientists (sampling by replica method, where only primary deoxidation products were selected [5, 6, 21, 22]). In these works, the impact of diffusion processes on the deoxidation reaction kinetics was almost completely excluded. Therefore, the results reflect the maximum deoxidizing capacity of titanium in the liquid melt. According to these authors, at a temperature of 1600°C and the titanium content of 0.1%,  $(6-7.5) \cdot 10^{-4} \% [O]$  will be in equilibrium with it if the titanium content is 0.01% -  $(1.7-2.3) \cdot 10^{-3} \% [O]$ .

The lowest deoxidizing ability of titanium in the titanium dioxide formation was obtained in early works of D. Chipman, B.K. Lyaudisb, A.M. Samarin, K. Gattelir. According to their data, the deoxidation constant at 1600°C is  $K_{TiO_2}^{-1} = (1-4) \cdot 10^{-6}$ , and the equilibrium oxygen concentration of the titanium content of 0.1 and 0.01% will be  $(3-6) \cdot 10^{-3}$  and  $(3-6) \cdot 10^{-2} \% [O]$  respectively. G. Knyuppel explains titanium low deoxidizing ability, which was obtained by V.I. Yavovskiy, regardless of the use of modern methods of oxygen activity analysis (e.m.f. method), by melting pot material (magnesium oxide) effect on the titanium oxides activity [26]. Therefore, the equilibrium oxygen content calculated according to the thermodynamic data in the case of Ti<sub>3</sub>O<sub>5</sub> formation was  $2.1 \cdot 10^{-3}$  and  $9.7 \cdot 10^{-3} \% [O]$ , which was lower than the

measured values, at the titanium content of 0.1 and 0.01% respectively.

It should be noted that thermodynamic calculations data of deoxidation constants for each oxide (regardless of the method of their calculation) differ slightly. According to different authors, at a temperature of 1600°C, their value is relatively stable:  $K_{\text{TiO}_2}^{-1} = (5.1-7.0) \cdot 10^{-7}$ ,  $K_{\text{Ti}_3\text{O}_5}^{-1} = (4.1-4.6) \cdot 10^{-18}$ ;  $K_{\text{Ti}_2\text{O}_3}^{-1} = 2.7 \cdot 10^{-11}$ .

However, the Table does not include the thermodynamic analysis results of I.S. Kulikov [7], since they differ from the others by 3-4 orders of magnitude. For example, according to this author, at 1600°C iron deoxidation with titanium constants are  $K_{\text{TiO}_2}^{-1} = 8,16 \cdot 10^{-4}$ ,  $K_{\text{Ti}_3\text{O}_5}^{-1} = 2,51 \cdot 10^{-4}$ ;  $K_{\text{Ti}_2\text{O}_3}^{-1} = 2,1 \cdot 10^{-4}$ . Obviously, this is a technical error, since they give good results further, and especially, when determining of interaction parameters and existence boundaries of the titanium oxides. According to I.S. Kulikov's calculations, at 1600°C, the following titanium concentrations in the iron, %  $1.1 \cdot 10^{-4} - 5.0 \cdot 10^{-4}$ ;  $5.0 \cdot 10^{-4} - 0.3$ ;  $0.3-5.0$  and more than  $5.0$  correspond to the areas of  $\text{TiO}_2$ ,  $\text{Ti}_2\text{O}_3$ ,  $\text{Ti}_3\text{O}_5$  and  $\text{TiO}$  formation.

From our point of view, the studies by D. Yanke and B. Fisher using probes based on  $\text{ThO}_2 - \text{Y}_2\text{O}_3$  when measuring of oxygen activity are the most reliable. They show that at a temperature of 1600°C, in the titanium content range of 0.001-0.1%, the value of the equilibrium constant is  $K_{\text{Ti}_3\text{O}_5} = 7.41 \cdot 10^{18}$  (the inverse value  $1.35 \cdot 10^{-19}$ ), and in the Ti content range of 0.1- 3%, the value of the constant is significantly lower  $K_{\text{Ti}_2\text{O}_3} = 3.70^{11}$  (the inverse value  $2.70 \cdot 10^{-12}$ ).

As for the interaction parameters  $e_O^{\text{Ti}}$  and  $e_{\text{Ti}}^{\text{Ti}}$ , they should be treated with care. Interaction parameter  $e_{\text{Ti}}^{\text{Ti}}$ , which average value is 0.041, is relatively reliable. Effect of titanium on the oxygen activity is ambiguous. According to I.S. Kulikov's thermodynamic calculations, the value of the interaction parameter  $e_O^{\text{Ti}}$  depends on the composition of the deoxidation products and is  $e_O^{\text{Ti}} = -0.69$  for  $\text{FeO} \cdot \text{TiO}_2$ ,  $e_O^{\text{Ti}} = -0.178$  for  $\text{TiO}_2$ ,  $e_O^{\text{Ti}} = -0.30$  for  $\text{Ti}_3\text{O}_5$ ,  $e_O^{\text{Ti}} = -0.37$  for  $\text{Ti}_2\text{O}_3$ .

However, according to experimental researches, this parameter value changes

significantly, even within the formation of one and the same oxide. If we exclude from the analysis the data of Z. Buzhek, A. Khutla, A. Smeli, Kh. Bell, which differ from the others, at the titanium content less than 0.2%, the interaction parameter will be  $e_O^{\text{Ti}} = - (0.160 - 0.187)$  in the case of  $\text{TiO}_2$  formation, and it will be  $e_O^{\text{Ti}} = - (0.31 - 0.37)$  in the case of  $\text{Ti}_3\text{O}_5$  formation. If the concentration of titanium in the liquid melt is more than 0.2% ( $\text{Ti}_2\text{O}_3$  formation), its effect on the oxygen activity increases, the interaction parameter is increased almost two times and will be  $e_O^{\text{Ti}} = - (0.65 - 0.75)$ .

We have analyzed the influence of the parameter  $e_O^{\text{Ti}}$  on the oxygen activity coefficient  $\lg f_o = e_O^{\text{Ti}} \cdot [\text{Ti}]$ , which is shown in Fig. 2, in order to evaluate the effect of titanium on oxygen activity in the liquid melt more objectively. Four parameter values are selected:  $e_O^{\text{Ti}} = - 0.187$  ( $\text{TiO}_2$  formation [14]),  $e_O^{\text{Ti}} = 0.31$  ( $\text{Ti}_3\text{O}_5$  formation [24]),  $e_O^{\text{Ti}} = - 0.8$  ( $\text{TiO}_2$  formation [18]),  $e_O^{\text{Ti}} = - 5.0$  ( $\text{Ti}_3\text{O}_5$  formation [22, 23]).

According to the analysis results, in the titanium concentration range of less than  $1 \cdot 10^{-2}$  % and the value of the parameter  $e_O^{\text{Ti}}$  of up to 0.8 units, and also at titanium concentration range of 0.01-0.1% and value of  $e_O^{\text{Ti}}$  up to 0.6 units within the analysis error, the oxygen activity will correspond to its concentration (activity coefficient of oxygen in the liquid melt is  $f_o = 0.9 - 0.98$ ).

In view of the above, it becomes clear why the equilibrium oxygen content of the titanium concentration in the range 0.001 - 0.1% for most researchers is similar regardless of the deoxidation constants and the interaction parameters  $e_O^{\text{Ti}}$  differences. At higher titanium concentrations, the liquid melt structure is a gradual changed (forming of complex compounds of ionic type and intermetallic compounds is possible), and the oxygen activity will be reduced.

Under interaction parameters recommended in the works of Z. Buzheko and A. Hutla, the liquid melt structural changes obviously occur much earlier, less than 0.01%. Unfortunately, in these papers, the mechanism

of this influence is not discovered. Nevertheless, the iron deoxidation with titanium at 1600°C isothermal line of these authors shown in Fig. 1 correspond well to the deoxidation isothermal lines of other authors, including the thermodynamic analysis results of I.S. Kulikov.

The oxygen activity coefficient is reduced at the titanium content of more than 0.1% due to the liquid melt structural changes and the formation of intermediate oxidation phases of variable valence; and consequently, the activity will be less than its concentration. Therefore, experimental data differ significantly from each other (sometimes by the order), and the equilibrium oxygen content is  $8 \cdot 10^{-4} - 4 \cdot 10^{-3}\%$ .

At higher titanium concentrations, the oxygen activity (activity coefficient decreases to  $f_o = 0.2 - 0.5$ ) is reduced faster than its concentration. According to numerous experimental data, there is a minimum, after which the titanium deoxidizing ability is reduced, and the equilibrium oxygen content is conversely increased as when aluminum deoxidizing.

The oxygen solubility is minimal at the titanium content in metal of about 1%. According to I.S. Kulikov, it is  $4.96 \cdot 10^{-4}\%$ ; according to D. Yanke and W. Fisher, it is  $2 \cdot 10^{-4}\%$ ; according to V.I. Yavoyskiy, it is  $1 \cdot 10^{-3}\%$ ; according to D. Chipman, it is  $1.64 \cdot 10^{-3}\%$ . With further increase in the titanium content, the equilibrium concentration of oxygen is increased significantly. It should be noted that the actual oxygen content in the liquide melt after deoxidation

with titanium is significantly higher than the equilibrium calculated by the conditions. This is a consequence of the kinetic stopping of reaction of deoxidation with titanium and its discharge on formation of a number of intermediate phases, including oxynitrides, unaccounted when calculating. According to [11], the oxygen content at the metal interface, including non-metallic inclusions, is on average 0.035%.

Thus, titanium is a strong deoxidizer. In accordance with its deoxidizing ability, it is located between the aluminum and the silicon. At a temperature of 1600°C and in the titanium content in metal of about 0.01%,  $(4-8) \cdot 10^{-3}\%$  of oxygen will be in equilibrium with it. At similar aluminum content, the equilibrium oxygen content will be much less than  $1 \cdot 10^{-3}\%$ . The advantage of titanium as deoxidizer is that deoxidation liquid products are formed at its content in the metal of up to 0.04%. This provides a sufficiently low content of soluble oxygen, and there are good conditions for deoxidation products floating.

However, considering the high cost of titanium (1.8 – 2.6 times higher than aluminum), it is practically not used as deoxidizer. The main purpose of titanium is the formation of highly dispersed structure and the hardening of steel by precipitation hardening mechanism. The preliminary metal deoxidation by stronger deoxidizer (aluminum) or carbon is carried out by vacuum-carbon deoxidation method in order to prevent oxidation and to increase the titanium assimilation degree. The last method is the most effective when smelting of microalloyed pure steels.

**Table 1.** Comparison of the literature data on the equilibrium of titanium and oxygen in molten iron

lgK	$K^{-1}$ (1600°C)	$e_O^{Ti}$	$e_{Ti}^{Ti}$	[Me], %	Method and reference
Titanium, reaction $[Ti]+3[O]+[Fe] \leftrightarrow FeTiO_3$					
42 260/T— 14.71	$1.4 \cdot 10^{-8}$	-0.069		0.01- 004	Calculated according to thermodynamic data of M.Ya. Medzhibozhskiy [12]
Titanium, reaction $[Ti]+2[O] \leftrightarrow TiO_2$					
30 700/T— 10.34	$8.93 \cdot 10^{-7}$	-	-	0.04-0.5	The additives of titanium in the molten iron; B.K. Lyaudis, A.M. Samarin [4]
	$1.28 \cdot 10^{-6}$	- 0.187	0.048	0.04-0.5	Analytical review according to data of Derge [13], performed by D.Chipman [14]
—	$5.81 \cdot 10^{-7}$	-	-	<1	E.m.f (MgO solution); V.P. Luzgin

					[15]
30 900/T— 10	$3.17 \cdot 10^{-7}$	-0.16	0.046	0.03-0.5	The equilibrium H <sub>2</sub> O/H <sub>2</sub> ; K. Suzuki [16]
—	$1.10 \cdot 10^{-6}$			<0.3	E.m.f (ZrO <sub>2</sub> —CaO solution); K. Gattelir [17]
36 600/T— 13.31	$5.88 \cdot 10^{-7}$	-0.80	0.05	-	Calculated according to thermodynamic data; Z. Buzhek , A. Khutla [18]
—	$2.80 \cdot 10^{-6}$	-	-	<0.3	Processing of literature data; E. Turkdogan [8]
33 740/T— 11.72	$5.08 \cdot 10^{-7}$	-	-	<0.0013	Calculated according to thermodynamic data; A. Zhakemo [19]
34 100/T- 12.089	$7.63 \cdot 10^{-7}$	-0.178	-	>0.04	Calculated according to thermodynamic data; M.Ya. Medzhibozhskiy [12]
Titanium, reaction $3[\text{Ti}]+5[\text{O}]\leftrightarrow \text{Ti}_3\text{O}_5$					
-	$3.50 \cdot 10^{-18}$	-0.37	-	0.0001- 0.4	The additives of titanium in the molten iron; E.Koyma [20]
41 500/T— 3.4	$1.75 \cdot 10^{-19}$		0.033	0.003- 0.2	The equilibrium H <sub>2</sub> O/H <sub>2</sub> , sampling by the replica method; K.Segava [21]
41 470/T— 3.4	$1.8 \cdot 10^{-19}$	-0.158		0.001- 0.2	Analytical review; Chino and Vada [5]
90 750/T— 29.15	$5.00 \cdot 10^{-20}$	-5.0	0.029	0.002-2	The equilibrium H <sub>2</sub> O/H <sub>2</sub> ; A. Smeli, Kh.Bell [22]
—	$2.80 \cdot 10^{-18}$	-4.8	-	0.007- 0.2	K' as a function of [%Ti]; Z. Buzhek [23]
—	$8.00 \cdot 10^{-17}$	-0.31	0.042	0.013- 0.25	Equilibrium ferrotitanium melt - titanium oxide; K. Suzuki, K. Sanbondzhi [24]
87 020/T— 29.12	$4.57 \cdot 10^{-18}$	-	-	0.013- 0.09	Calculated according to thermodynamic data; A.Zhakemo [19]
—	$1.35 \cdot 10^{-19}$	-	-	0.001- 0.1	E.m.f measurement (ThO <sub>2</sub> —Y <sub>2</sub> O <sub>3</sub> solution); D. Yanke, V. Fisher [25]
77 700/T— 24.1	$4.12 \cdot 10^{-18}$	-	-	0.008- 0.2	Calculated according to thermodynamic data; V.I. Yavoyskiy [9]
93 000/T— 33.6	$8.85 \cdot 10^{-17}$			0.008- 0.2	E.m.f measurement (MgO solution); V.I. Yavoyskiy [9]
Titanium, reaction $2[\text{Ti}]+3[\text{O}]\leftrightarrow \text{Ti}_2\text{O}_3$					
	$1.25 \cdot 10^{-10}$	-0.65	-	0.24- 3.6	E.m.f (MgO solution) V.I. Yavoyskiy [9]
—	$4.10 \cdot 10^{-11}$	-0.75	-	0.25-3	K' as a function of [%Ti]; Z. Buzhek [23]
53 280/T- 17.88	$2.72 \cdot 10^{-11}$	-	-	<0.9	Calculated according to thermodynamic data; A.Zhakemo [19]
—	$2.70 \cdot 10^{-12}$	-	0.048	0.1-8.8	E.m.f measurement (ThO <sub>2</sub> —Y <sub>2</sub> O <sub>3</sub> solution); D. Yanke, V. Fisher [25]
48800/T- 15.5	$2.78 \cdot 10^{-11}$	-0.65	-	0.2-1	Calculated according to thermodynamic data; V.I. Yavoyskiy [9]

-	$2.32 \cdot 10^{-12}$	-	-	0.2-2	The equilibrium $H_2O/H_2$ , replica method, thermodynamic correction for $Ti_2O_3$ ; K.Segava [21]
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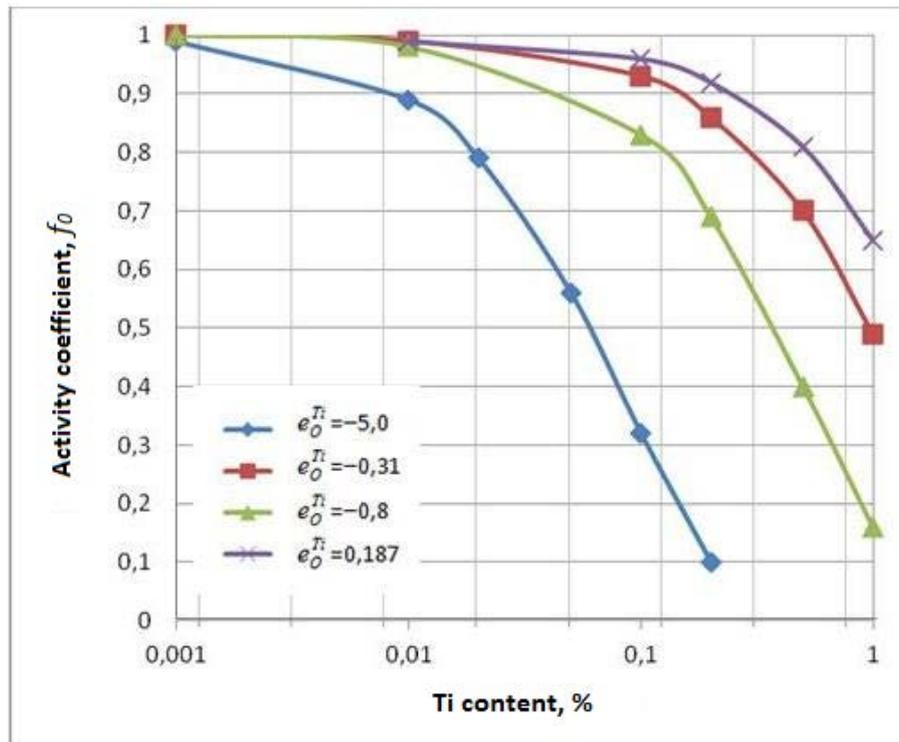


Figure 1. Effect of interaction parameters on the activity coefficient of oxygen in the molten Fe-Ti-a

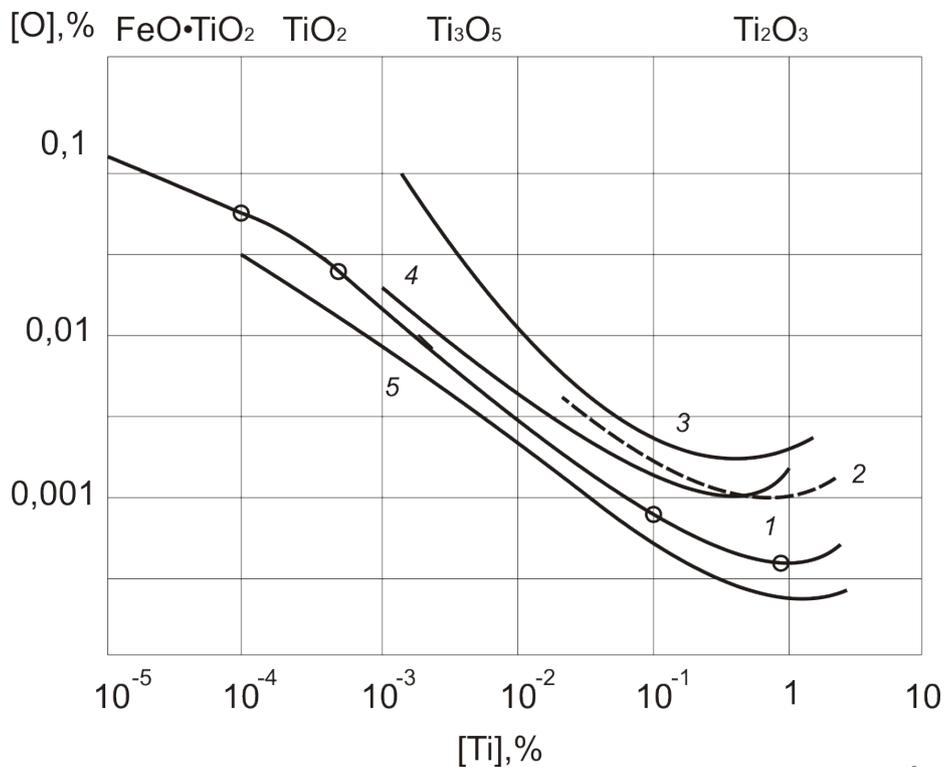


Figure 2. The dependence of the oxygen concentration in the iron on titanium content at 1600°C according to different authors:

1 - I.S. Kulikov [7]; 2 - V.I. Yavoyskiy [9]; 3 - D. Chipman [14]; 4 - Z. Buzhek and A. Khutla [18]; 5 - D. Yanke and V. Fisher [25]; • - Suzuki [24]; x - Koyma [20].

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