ARCHIVES OF METALLURGY AND MATERIALS
Volume 56 2011 Issue 3

DOI: 10.2478/v10172-011-0069-x

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SIMULATION OF OXYGEN AND NITROGEN REMOVAL FROM STEEL BY MEANS OF TITANIUM AND ALUMINUM

SYMULACJA USUWANIA TLENU I AZOTU ZE STALI PRZY UŻYCIU TYTANU I GLINU

Authors' computer program was employed in the simulation of the course of steel refining by means of simultaneously used aluminium and titanium. The mass and chemical composition of liquid steel and non-metallic precipitates, were calculated at constant or variable temperature. The influence of assumed nitrides form on the results of simulation was determined. Nitrides may be considered either as separate phases or as the components of non-metallic solution. The stoichiometry of titanium oxide obtained also influences the results of simulation. Parallel analysis of steel refining was carried out with the use of FactSage program. As a result of calculations the subsequent states of equilibrium between steel and non-metallic phase were determined. It was found that aluminium and titanium nitrides may exist only as the components of oxide-nitride solution, not as separate phases.

Keywords: steel refining, computer simulation, aluminium, titanium, nitrides, oxides

Przy pomocy własnego programu komputerowego dokonano symulacji przebiegu rafinacji stali przy pomocy glinu i tytanu, wyznaczając masę i skład chemiczny ciekłej stali i wydzieleń niemetalicznych dla ustalonej lub zmiennej temperatury. Rozpatrzono konsekwencje występowania dwóch możliwych form istnienia azotków glinu i tytanu: jako odrębnych faz i jako składników ciekłego roztworu. Również stechiometria tlenku tytanu uzyskanego w wyniku odtleniania wpływa na wynik obliczeń. Równoległą analizę tego samego przypadku przeprowadzono przy pomocy programu FactSage, wyznaczając kolejne stany równowagi między ciekłą stalą a fazą niemetaliczną. Stwierdzono, że azotki glinu i tytanu mogą występować tylko jako składniki roztworu tlenkowo-azotkowego., nie zaś jako odrębna faza.

1. Introduction

Aluminum and titanium are frequently introduced jointly into liquid steel. In alloyed and micro-alloyed steels fine precipitates of titanium compounds as nitrides or carbo-nitrides play double role: inhibition of grain growth during heating prior to the hot rolling operation as well as they promote precipitation hardening. During titanium introduction into liquid steel part of it is lost in the form of slag. Nitrides and oxides which form during ladle treatment of liquid steel, and most of these which form during solidification, are useless from the view-point of grain control.

Aluminum affinity to oxygen and nitrogen is comparable to this of titanium, so aluminum oxide and nitride are simultaneously formed, what reduces losses of titanium. The titanium level in the steel has to be precisely set during ladle treatment, so the control of titanium behaviour is of considerable importance. Besides, the cost of titanium has to be taken into account as well.

Present work is aimed at mathematical description and simulations of titanium and aluminium behaviour in the above processes. The basic data regarding thermodynamic relations describing the problem was already discussed in several publications [1-5]. The present authors recently studied the behaviour of titanium and aluminium in two types of steel. The typical equilibrium approach was used in the publications [6] and [7], where the sequence of states of thermodynamic equilibrium between liquid steel and liquid oxide precipitates was determined. The basic composition of steel, mainly the content of silicon and manganese influences the composition of oxide precipitates, what in turn determines their physical form: solid or liquid. At high concentrations of Al_2O_3 the precipitates are solid, prone to large clusters formation, what influences their floating ability.

Thus the influence of basic steel composition as well as the level of oxygen and nitrogen on the mass and composition of precipitates has to be established on the ground of equilibrium thermodynamics and kinetic cal-

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TABLE 1

Chemical composition (mass %) of AH-36-3u steel according to PN-93/H-92147 Polish standard

C	Mn	Si	P	S	Al	Cr	Ni	Cu	Mo	V	Ti
0.15 – 0.18	1.45 – 1.60	0.15 – 0.25	0.025 max	00.012 max	0.02 – 0.07	0.15 max	0.2 max	0.2 max	0.08 max	0.01 – 0.03	0.008 – 0.02

TABLE 2

Mass of steel components assumed for the simulation of steel refining (kg)

Fe	Mn	Si	O	N	Al	C	Ti
300 000	4 000	450	15	15	20 -30 -40- 50 - 60	450	50 – 100

culations. On the other hand, the simpler simulation program is also of some value in prediction of the composition of precipitates. Besides it can be employed in process simulation, if kinetic parameters are taken into account.

The aim of the present work is the simulation of simultaneous action of titanium and aluminum by means of two procedures in order to obtain better picture of non-metallic precipitates formation and their composition.

2. Object of simulations

The simulation of steel refining was carried out for AH-36-3u steel, assigned for ship constructions, of chemical composition according to Polish standard PN-93/H-92147 as presented in Table 1.

3. The results of simulations obtained by means of FactSage package

The simulation of the influence of aluminum and titanium additions on the parameters of thermodynamic equilibrium between liquid steel and non-metallic phase was carried out by means of FactSage system, program Equilibrium [8]. The simulation consists in determination of subsequent equilibrium states for various additions of aluminum and titanium. The total mass of system components is given in Table II, where two versions of mass of titanium and five version of mass of aluminum are given, which were taken alternatively in calculations.

The thermodynamic database of FactSage program used in the present work suggests the parallel formation of two titanium oxides: TiO_2 and Ti_2O_3 as the result of reaction between titanium and oxygen dissolved in liquid steel. The nitrides of aluminum and titanium that might arise are treated as the separate phase. The results of calculations are presented in Figs 1 and 2, which concern the components of liquid steel, and in Figs 3-5, which concern the components of liquid non-metallic phase.

The evolution of aluminum concentration in liquid steel resulting from the addition of Al and Ti at constant temperature 1810 K was demonstrated in Fig. 1.

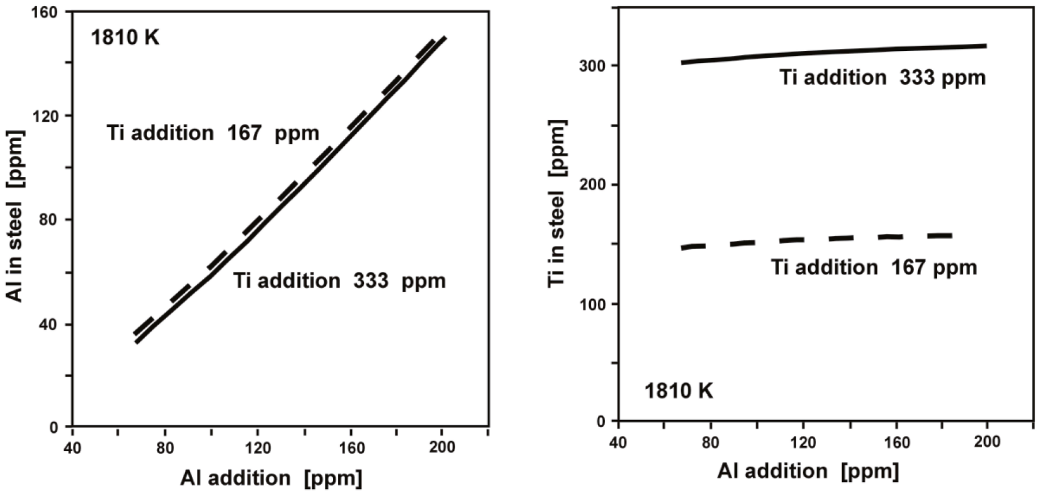

Fig. 1. The variation of aluminum and titanium concentration in liquid steel as a result of introduction these elements to the system at 1810 K (equilibrium calculations)

It may be noticed that the influence of amount of aluminum added on its concentration in steel only slightly deviates from linear dependence, as major part of added aluminum dissolves in liquid steel. The influence of titanium level on aluminum concentration is very weak. As titanium and aluminum compete in bonding with oxygen and nitrogen, higher titanium concentration corresponds to slightly lower aluminum concentration.

As may also be seen from Fig. 1, the concentration of titanium in steel grows very slightly with aluminum addition, as a result of partial reduction of titanium oxides.

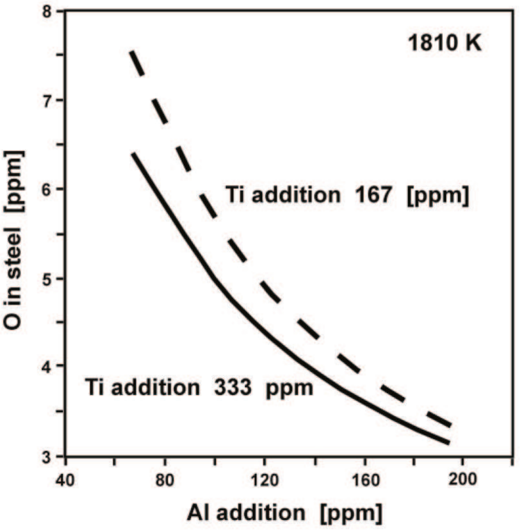

Fig. 2. The variation of oxygen concentration in liquid steel as a result of aluminum and titanium introduction to the system at 1810 K (equilibrium calculations)

The influence of aluminum and titanium additions on oxygen concentration in liquid steel at 1810 K is demonstrated in Fig. 2. Strong deoxidizing action of both aluminum and titanium may be observed. As a result, final oxygen concentration in solution may be as low as 3 ppm.

Figures 3-5 present the evolution of the composition of non-metallic liquid solution phase composed of oxide precipitates. Fig. 3 concerns the concentrations of FeO and MnO, which fall rapidly with increasing amount of Al added. At Al addition as high as 200 ppm the FeO concentration reaches 0.15 mass %, while MnO concentration – 1 mass %. It should be noticed that this behaviour correlates well with the variation of oxygen concentration in steel. Both oxides, FeO and MnO are easily reduced with aluminum and titanium. However, the reducing action of titanium is weaker.

Fig. 4 presents the changes of SiO_2 and Al_2O_3 concentrations in liquid oxide phase as a function of the amount of aluminum and titanium added. The diverse trends may be observed. The silicon affinity towards oxygen is considerably weaker than this of aluminum and titanium, that's why SiO_2 is partly reduced through both aluminum and titanium. Decreasing concentration of SiO_2 attains finally stable level of 0.2 mass %. Aluminum oxide reveals opposite behaviour. Aluminum addition into the system results in the increase of Al_2O_3 concentration at the expense of other oxides, whereas addition of titanium results in decrease of Al_2O_3 concentration.

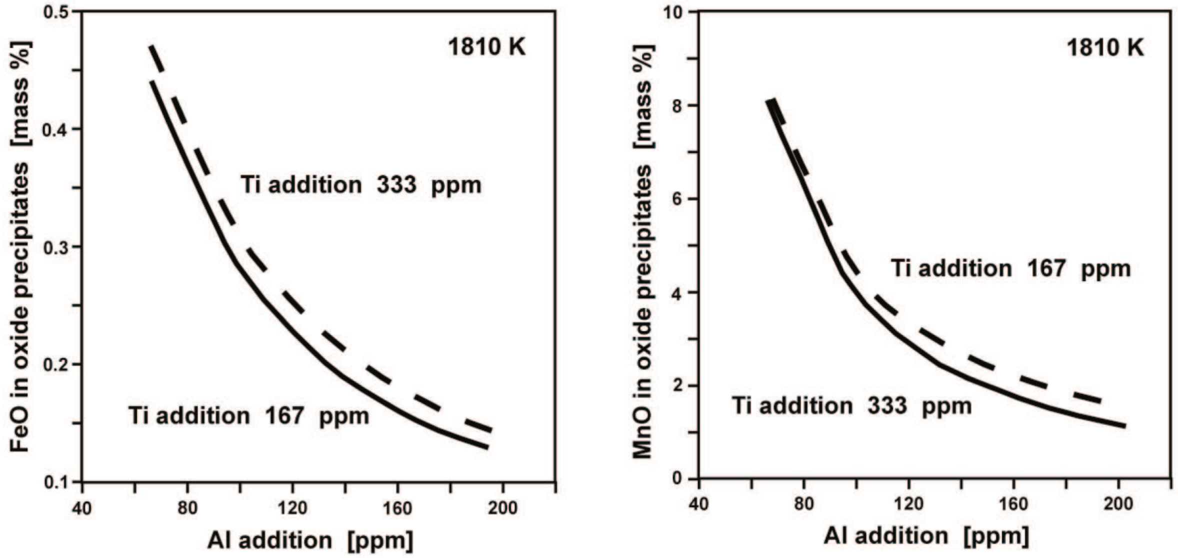

Fig. 3. The variation of FeO and MnO concentration in liquid steel as a result of aluminum and titanium introduction to the system at 1810 K (equilibrium calculations)

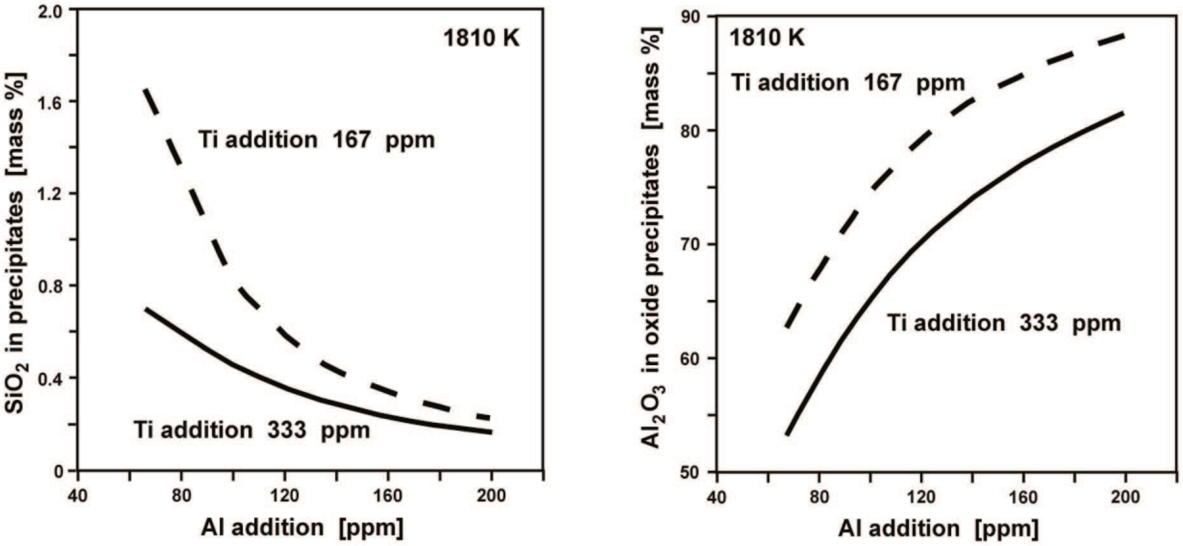

Fig. 4. The variation of SiO_2 and Al_2O_3 concentration in liquid steel as a result of aluminum and titanium introduction to the system at 1810 K (equilibrium calculations)

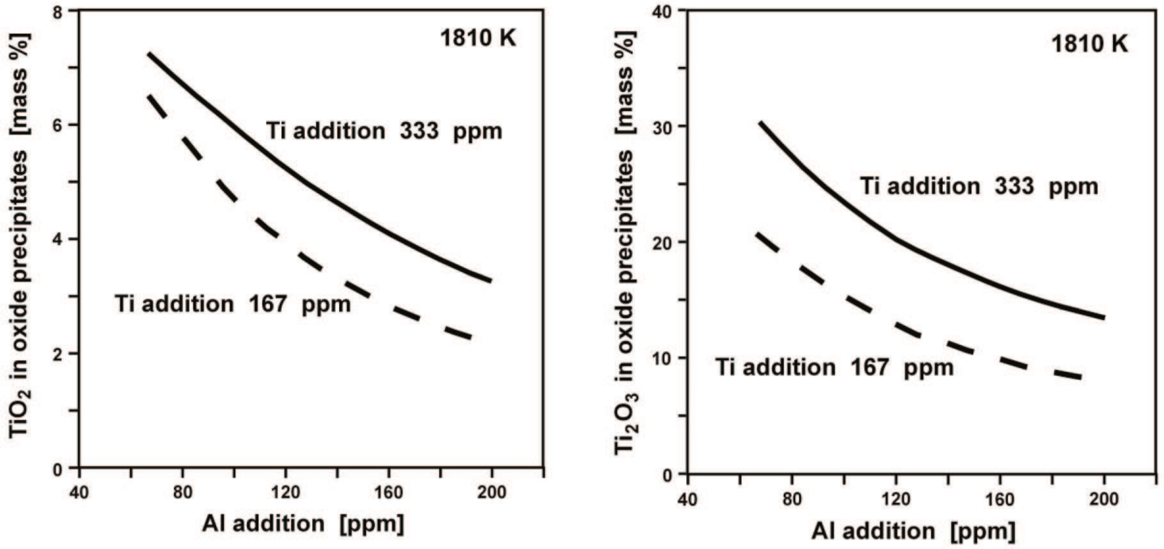

Fig. 5. The variation of TiO_2 and Ti_2O_3 concentration in liquid steel as a result of aluminum and titanium introduction to the system at 1810 K – the results of equilibrium calculations

Fig. 5 presents the dependences of the contributions of titanium oxides: TiO_2 and Ti_2O_3 in liquid oxide phase on the amount of aluminum and titanium added. The occurrence of these titanium oxides is imposed with FactSage database. It has to be noticed that three titanium oxides may occur: Ti_2O_3, Ti_3O_5 i TiO_2.

As it is suggested by [3], at the temperature 1873 K and at titanium concentrations within the range 10^{-3} mass % up to several mass % , the oxide Ti_3O_5 is stable at lower titanium concentration, while TiO_2 – at higher concentrations. The boundary value is 0.25 mass % Ti. The above is valid at high oxygen activities in steel, corresponding to saturation at given temperature and composition. Formation of TiO_2 requires higher values of oxygen concentration, which is possible in the presence of steel components, which increase oxygen activity, as manganese.

It may be seen from Fig. 5 that maximum value of TiO_2 is 7 mass %, while this of Ti_2O_3 – 30 mass %. The concentration of both titanium oxides decreases with addition of aluminum, and it increases with addition of titanium.

It is characteristic that the results of equilibrium calculations by means of FactSage package did not indicate the presence of titanium nitride in liquid non-metallic phase. It seems to be the result of the structure of equilibrium module of FactSage, which takes into account two separate non-metallic solutions of oxides and nitrides. The probable reason for such approach is lack of coherent model of ionic solution composed of oxide and nitride anions.

4. Simulations of steel deoxidization with the use of WYK-STAL software

4.1. Program construction

Simulation program of steel refining adopted in the present work, is based on the former version WYK_STAL of Iwanciw [9]. It is designed for simulation and real time assistance of ladle refining of steel. The program calculates subsequent states of equilibrium for the system composed of liquid steel, non-metallic precipitates, liquid slag and gas.

Initially the system under consideration contains only liquid steel of defined mass, chemical composition and temperature. Then the ferroalloys are introduced in one batch or in the specified portions. Continuous introduction of the reagent is also possible. An average duration of tapping operation for 140 Mg converter (Arcelor Mittal Kraków) is 6 min, while for 300 Mg converter (Arcelor Mittal Katowice) – 8 min.

During tapping the reactions between steel components and the introduced ferroalloys proceed very rapidly, as the system is vigorously stirred with the energy of falling steel stream. The reactions proceeding in the system may be considered as the oxidization of steel components. Non-metallic precipitates produced in these reactions swim out to the top slag, Inclusions and slag are treated as the ionic solutions, predominantly composed of oxides. However, the program can be used for simulation of further production steps, where the deoxidizers are added to steel. The reaction of the deoxidizer dissolved in steel with dissolved oxygen may be generally presented as:

$$m\,[R] + n\,[O] = R_mO_n \tag{1}$$

The product of reaction (1) – the oxide R_mO_n is either dissolved in the liquid oxide phase or is present as pure solid oxide of Raoultian activity equal 1.

The equilibrium constant of reaction (1):

$$K_{(1)} = \frac{X_{R_mO_n} \cdot \gamma_{R_mO_n}}{([\%R] \cdot f_R)^m \cdot ([\%O] \cdot f_O)^n} \tag{2}$$

where f_R i f_O are the Henrian activity coefficients for the concentrations [%R] i [%O] expressed in mass %,

$X_{R_mO_n}$denotes the mole fraction of the compound R_mO_n In liquid oxide solution, and $\gamma_{R_mO_n}$ – Raoultian activity coefficient of this oxide.

The task of the program is the calculation of current mass and chemical composition of reacting phases at any point of the process. The evolution of concentrations of steel components is described with simple first order kinetic equation.

$$\frac{dC}{dt} = -k \cdot \left(C - C_{eq}\right) \tag{3}$$

where: C_{eq} is the equilibrium concentration of component at given oxygen level in solution, k is the rate constant

Such equation is set up for each potential reagent. The total rate of deoxidization process is strongly influenced with hydrodynamic conditions, which result from stirring intensity and reactor geometry. According to classical approach, the transport of reagent to the reaction site is composed of two stages: convective transport of component within the bulk flow of liquid steel, and diffusive transport of component through the boundary layer. The concentration of both oxygen and deoxidizing agent varies across the boundary layer from average current values for liquid steel to the values corresponding to equilibrium of reaction (1). Basing on the above assumptions the following form of kinetic equation for deoxidization was used in the publication [9].

$$\frac{d\,[\%O]}{dt} = B_m \cdot D_R \cdot ([\%O] - [\%O]_{rwn}) \tag{4}$$

where: [%O] – the average oxygen concentration In liquid steel (mass %),

$[\%O]_{eq}$ – the oxygen concentration corresponding to the equilibrium of reaction (1) at current average concentration of deoxidizer [%R]

B_m – the average value of overall mixing coefficient in the reaction system,

D_R – diffusion coefficient of the deoxidizer R, which takes into account the atomic mass ratio and the stoichiometric coefficients in reaction (1).

The solution of equation (4) is as follows:

$$[\%O]_t = [\%O]_{eq} + ([\%O]_0 - [\%O]) \cdot \exp\left(-B_m \cdot D_R \cdot t\right) \tag{5}$$

where: $[\%O]_t$ – average current oxygen concentration in liquid steel

$[\%O]_0$ – initial average oxygen concentration In liquid steel.

In the numerical simulation of the process the values $[\%O]_0$ and $[\%O]_t$ refer to the beginning and the end of the time step.

The program module based on equations (3) – (5) expresses the process rate for each individual metal as a function of deviation of dissolved oxygen concentration from its equilibrium value. The kinetic equation applied does not include the process mechanism.

The precipitates formed as a result of deoxidization swim out from liquid steel. In every case the larger particles swim out faster. Thus the growth and agglomeration mechanisms play very important role. In the present program very simple model of removal of oxide precipitates from steel was adopted.

For the purpose of the present work the program was extended to deal with the simultaneous precipitation of nitrides and oxides. The database of nitrides formation containing free energy changes of reactions and Wagner – Chipman interaction parameters was also added. Additionally, the fragment of database regarding titanium oxides and interaction parameters of titanium and nitrogen was also updated, including the available information up to 2008 [1-5].

4.2. Results of simulations

The subject of simulation was to trace the evolution of the mass and chemical composition of oxide – nitride precipitates with time and temperature. The simulation assumes the following course of process:

1. Simultaneous introduction of 60 kg of aluminium and 50 kg of titanium in one batch,
2. Equilibration of the system at 1810 K,
3. Lowering the temperature to 1790 K,
4. Equilibration of the system at 1790 K.

In further calculations higher amounts were also taken into account.

The results of simulations are presented in Figs 6-9. Fig. 6 shows, how titanium and aluminium added to liquid steel are distributed between liquid metal, oxide phase and nitride phase. It was assumed in this variant of simulation that titanium is bonded with oxygen in the form of Ti_3O_5. What regards the nitrides, two possibilities were included in calculations. The distribution of aluminum and titanium were calculated for two alternatives:

a. TiN and AlN were assumed as the components of oxide – nitride ionic ideal solution, and their activities were equal to molar fractions,
b. TiN and AlN were regarded as separate phases; thus their activities were equal to 1.

For comparison the result of equilibrium calculation by means of FactSage package are included (narrow column marked as F).

The results of simulations show the distinct influence of two options presented above on titanium distribution. If TiN is treated as the component of ionic solution, it contains ca 5% of total titanium mass, while merely 1% of titanium in the system is in the form of oxide.

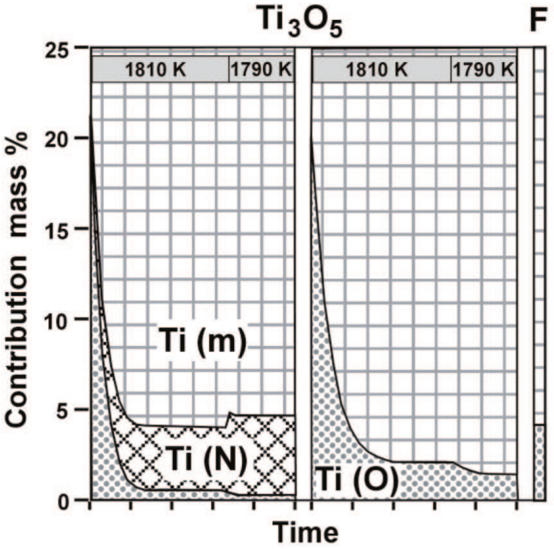

Fig. 6. Distribution of titanium as a result of simultaneous aluminum and titanium deoxidization at 1810 and 1790 K. Results of calculation according to assumptions: a) (left) $a_{MeN} = X_{MeN}$, and b) (right) $a_{MeN} = 1$. F – result of calculation with the use of FactSage. Ti oxide form is Ti_3O_5

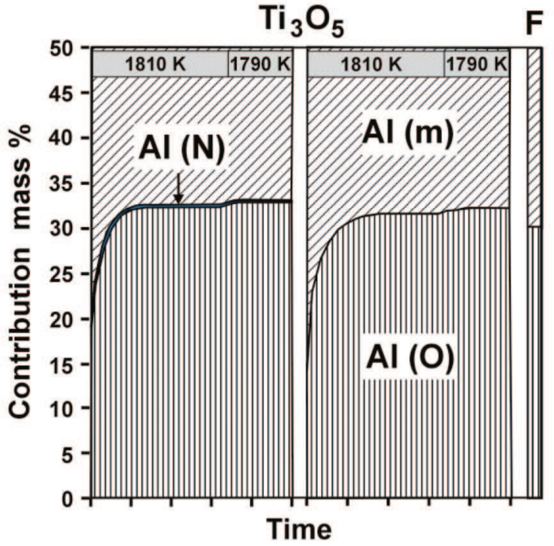

Fig. 7. Distribution of aluminum as a result of simultaneous aluminum and titanium deoxidization at 1810 and 1790 K. Results of calculation according to assumptions: a) (left) $a_{MeN} = X_{MeN}$, and b) (right) $a_{MeN} = 1$. F – result of calculation with the use of FactSage. Ti oxide form is Ti_3O_5

If titanium nitride is considered a separate phase, it does not appear as the result of simulation. Instead, the fraction of titanium bonded with oxygen is higher, ca 3 mass %.

The distribution of aluminium between metal, oxide and nitride considerably differs from this of titanium, Aluminum bonded as Al_2O_3 exceeds 30 % of total Al mass added to the system, while AlN appears in very low amount only if TiN is dissolved in ionic solution. If TiN forms as a separate phase, no free nitrogen remains for AlN formation.

The simulation of process includes also the temperature decrease from 1810 K to 1790 K, which to some extent corresponds to the progress of process, e.g. argon purging. This temperature change is reflected by the distribution of titanium and aluminum between three phases. In the case of titanium its mass in liquid steel slightly grows with temperature decrease, while in the case of aluminum its mass in steel decreases. This effect may be simply explained as a result of titanium oxide reduction with aluminium.

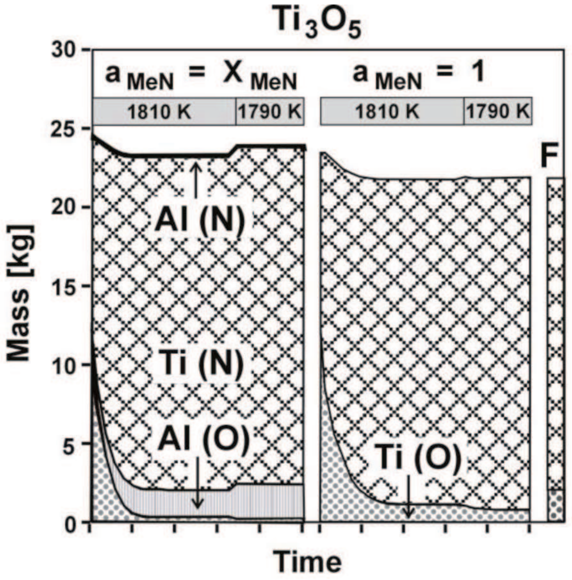

Fig. 8. Comparison of mass of non-metallic products of simultaneous aluminum and titanium deoxidization at 1810 and 1790 K.
Ti oxide form is Ti_3O_5.
Results of calculation according to assumptions: a) $a_{MeN} = X_{MeN}$, and b) $a_{MeN} = 1$. F – the result of calculation by means of FactSage

Fig. 8 presents the comparison of mass proportion of non-metallic products of deoxidization for the case of Ti_3O_5 formation. Left hand side of the diagram is obtained under assumption:$a_{MeN} = X_{MeN}$, while the right hand side under assumption: $a_{MeN} = 1$.

It may be seen from Fig. 8, that the assumption made on the behaviour of nitrides of titanium and aluminum determines the results of calculations. Occurrence of pure nitrides TiN or AlN is thermodynamically improbable at the temperatures and nitrogen concentrations taken into consideration. On the other hand, considerable amount of TiN and small amount of AlN dissolved in oxide phase may exist.

Figs 6-8 present also the results of equilibrium calculations carried out with FactSage package, which assumed nitrides as the separate phases. In this case titanium and aluminum nitride do not appear in the results of calculations. Thus the calculations by means of FactSage can only yield the distribution of titanium and aluminum between steel and oxide phase.

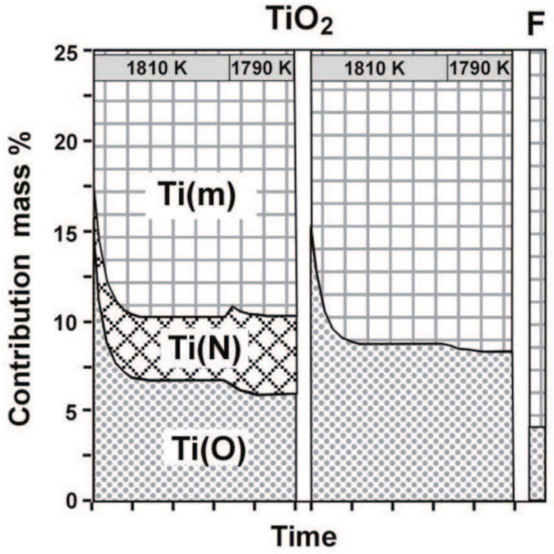

Fig. 9. Distribution of titanium as a result of simultaneous aluminum and titanium deoxidization at 1810 and 1790 K. Results of calculation according to assumptions: a) (left) $a_{MeN} = X_{MeN}$, and b) (right) $a_{MeN} = 1$. F – result of calculation with the use of FactSage. Ti oxide form is TiO_2

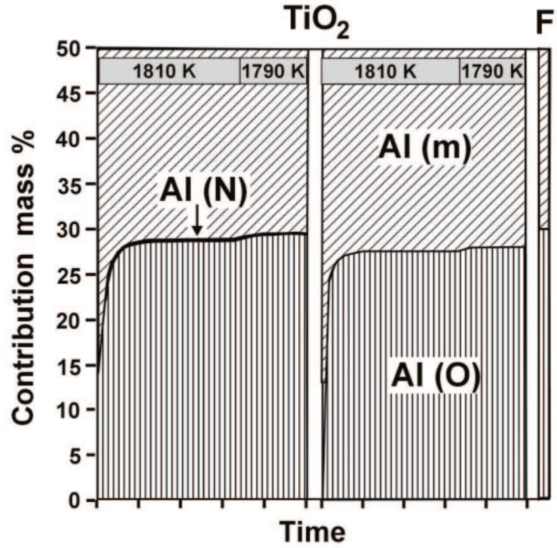

Fig. 10. Distribution of aluminum as a result of simultaneous aluminum and titanium deoxidization at 1810 and 1790 K. Results of calculation according to assumptions: a) (left) $a_{MeN} = X_{MeN}$, and b) (right) $a_{MeN} = 1$. F – result of calculation with the use of FactSage. Ti oxide form is TiO_2

Fig. 9 and 10 present the distribution of titanium and aluminum between phases existing in the system in the case, if titanium is bonded in the form of TiO_2. Similarly to the variant with Ti_3O_5 formation, evidently higher amount of titanium nitride is obtained under assumption that TiN is a component of non-metallic solution. In such case ca 5% of total titanium amount is bonded as the nitride. Comparison with Fig. 6 reveals that the amount of titanium bonded with oxygen is much larger for simulation variant with TiO_2 formation. If the TiN formation is assumed, the fraction of titanium bonded with oxygen exceeds 5%; if TiN does not appear – almost 10% of total titanium is bonded with oxygen.

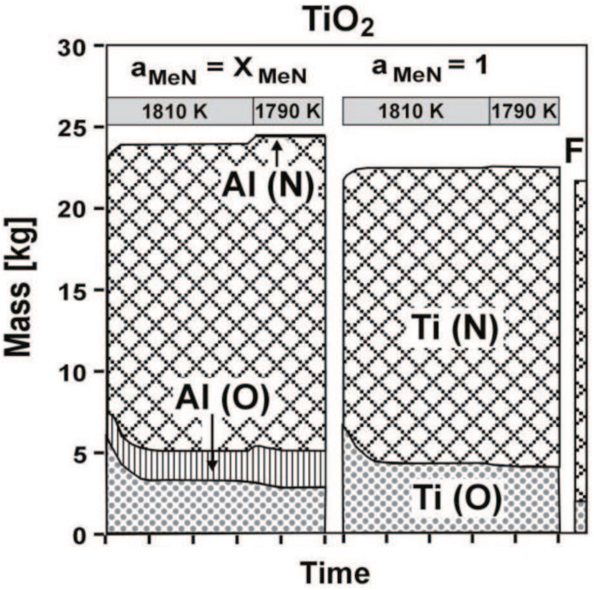

Fig. 11. Comparison of mass of non-metallic products of simultaneous aluminum and titanium deoxidization at 1810 and 1790 K.
Ti oxide form is TiO_2.
Results of calculation according to assumptions: a) $a_{MeN} = X_{MeN}$, and b) $a_{MeN} = 1$. F – the result of calculation by means of FactSage

Fig. 11 shows the comparison of mass proportions between oxides and nitrides of aluminum and titanium for two simulation variants. In the first variant (left hand side) the nitrides are the components of an ideal solution, while in the second (right hand side) they create the separate phase. The titanium nitride may emerge as a component of liquid non-metallic solution. The aluminum nitride also emerges in such conditions, but its amount is much less than this of titanium nitride. For comparison, the results of FactSage simulations yield somewhat lower participation of titanium oxide and somewhat higher part of aluminum oxide.

4.3. Calculations for variable aluminum additions

The simulations of the deoxidization process, in which variable addition of aluminum in the range 60-500 ppm was used, were also carried out with the procedure outlined above, by means of WYK_STAL program. The constant mass of titanium in steel, i.e. 50 kg, was assumed in this stage of calculations. The results are presented in Figs. 12-16. They regard the case of TiO_2 formation as the only oxide of titanium. Fig 12 shows the variation of mass of titanium dissolved in steel in the system containing 300 Mg of Fe. It may be seen that depending of aluminum addition the mass of titanium dissolved in steel varies by 4-5 kg, which is about 10% of total titanium amount. The assumptions regarding the form of nitrides (separate phase or component of solution), influence titanium amount in liquid steel. If nitrides are allowed to form, some quantity of titanium is bonded as TiN. It should be added, that calculation by means of FactSage yields considerably higher mass of Ti in liquid steel.

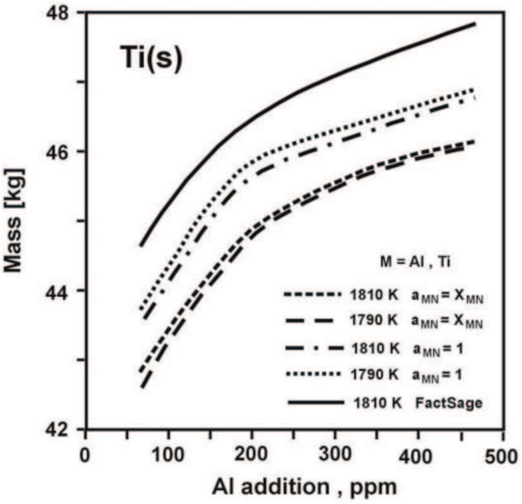

Fig. 12. Mass of titanium dissolved in liquid steel, calculated by means of WYK_STAL software at 1810 K and 1790 K under alternative assumptions of nitrides form. Titanium oxide assumed as TiO_2

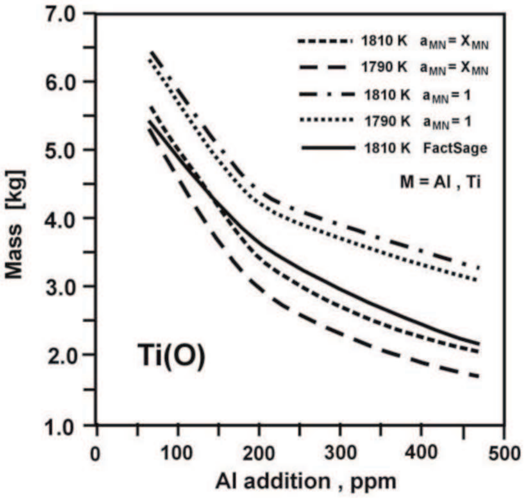

Fig. 13. Mass of titanium bonded as TiO_2, calculated by means of WYK_STAL software at 1810 K and 1790 K under alternative assumptions of nitrides form

Fig. 13 shows the mass of titanium bonded as TiO_2, At low aluminum addition about 5 kg of titanium is in the form of oxide. Higher addition of aluminum partly reduces the titanium oxide. In this case the curve obtained with FactSage falls close to results of FactSage calculations. The calculated amount of aluminum bonded as Al_2O_3 is presented in Fig. 14.

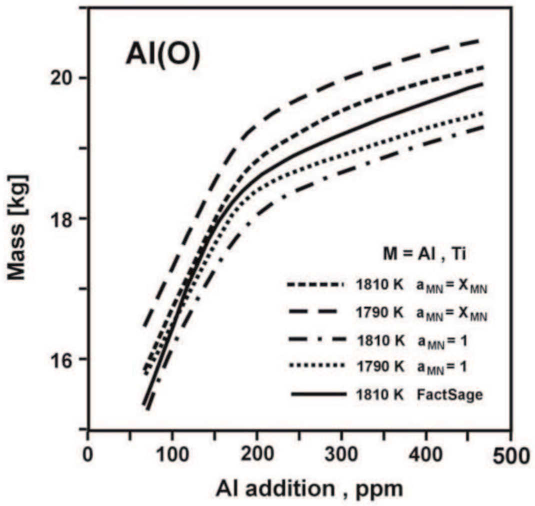

Fig. 14. Mass of aluminum bonded as Al_2O_3, calculated by means of WYK_STAL software at 1810 K and 1790 K under alternative assumptions of nitrides form. Titanium oxide assumed as TiO_2

This amount reaches 20 kg at the highest aluminum additions and cannot be exceeded due to the deficiency of oxygen dissolved in steel.

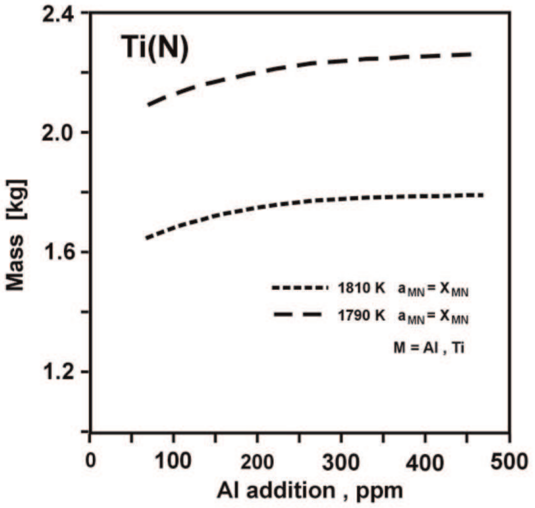

Fig. 15. Mass of titanium bonded as TiN, calculated by means of WYK_STAL software at 1810 K and 1790 K under alternative assumptions of nitrides form. Titanium oxide assumed as TiO_2

Figs. 15 and 16 present the mass of titanium and aluminum bonded in the form of nitrides. In this case only one variant of calculations may be employed, in which nitrides are dissolved in oxide solutions. Potential mass of titanium bonded in TiN is of the order 2 kg and does not change much with aluminum addition. The mass of aluminum bonded in AlN is much lower, but it strongly grows with increasing aluminum addition. In the case of nitrides formation the influence of temperature is important. The temperature fall results in enhanced nitrides formation.

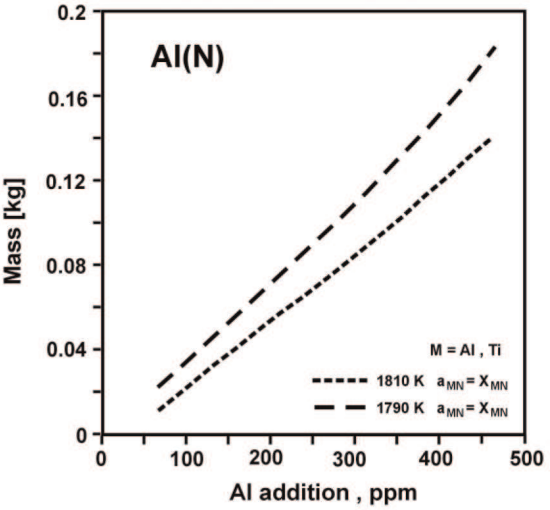

Fig. 16. Mass of aluminum bonded as AlN, calculated by means of WYK_STAL software at 1810 K and 1790 K under alternative assumptions of nitrides form. Titanium oxide assumed as TiO_2

5. Conclusions

The reliable simulation of steel refining processes, mainly deoxidization, must be based on the reliable determination of the equilibrium states of the system under consideration and the evolution of parameters of equilibrium with process duration. If steel refining process is restricted only to formation of metallic oxides as a result of reaction of deoxidizers with oxygen dissolved in steel, the determination of equilibrium parameters is considerably simple. If formation of sulphides and nitrides is also considered, the serious problems appear regarding the description of non-metallic phase. Insufficient data do not allow the unambiguous definition of the substances present in the system, and some important relations regarding components activities are lacking.

Present work is intended as the approach to this problem. It attempts to show, how the assumptions regarding the stoichiometry of oxides in the system as well as the presence of nitrides in non-metallic precipitation phase influence the course and results of deoxidization. The simulations in the present work were carried out with the use of two independent programs. Four variants were explored in the present work according to the assumptions concerning:

a) The stoichiometry of titanium oxide appearing in the system (TiO_2 or Ti_3O_5),
b) The form of appearance of nitrides AlN and TiN (in liquid oxide – nitride solution or as the separate phase).

The results obtained for these variants considerably differ between each other. If one expects TiN or AlN to form the separate phase, i.e. their Raoultian activities would be unity, then the calculations do not indicate the presence of these compounds in the system. In contrary, if one assumes the occurrence of TiN or AlN as the components of liquid solution, the calculations reveal the considerable amount of these substances in the system: several. mole pct of TiN and less than 1 mole pct of AlN in liquid solution.

The choice of titanium oxide stoichiometry (Ti_3O_5 or TiO_2) evidently affects the results of calculations, i.e. amount of appearing oxides and nitrides. In the case of Ti_2O_3 formation the mas sof titanium bonded with oxygen is considerably higher than In the case of TiO_2. The amount of aluminum bonded with oxygen to form Al_2O_3 shows the opposite tendency, i.e. is a little higher in the case of TiO_2.

This work was sponsored by the Ministry of Science as the statute work at AGH University of Science and Technolog in the years 2009-2010 (contract nr 11.11.110.937).

REFERENCES

[1] J.-J. Pak, J.-O. Jo, S.-I. Kim, W.-Y. Kim, T.-I. Chung, S.-M. SeO, J.-H. Park, D.-S. Kim, Thermodynamics of Titanium and Oxygen Dissolved In Liquid Iron Equilibrated with Titanium Oxides, ISIJ Intern. **47**, 16-24 (2007).

[2] W.-Y. Kim, J.-G. Kang, C.-H. Park, J.-B. Lee, J.-J. Pak, Thermodynamics of Aluminum, Nitrogen and AlN formation in Liquid Iron, ISIJ Intern. **47**, 945-954 (2007).

[3] W.-Y. Kim, J.-O. Jo, C.-O. Lee, D.-S. Kim, J.-J. Pak, Thermodynamic Relation between Aluminium and Titanium in Liquid Iron, ISIJ Intern. **47**, 17-22 (2007).

[4] J.-Y. Kim, J.-O. Jo, T.-I. Chung, D.-S. Kim, J.-J. Pak, Thermodynamics of Titanium, Nitrogen and TiN Formation in Liquid Iron, ISIJ Intern. **47**, 1082-1089 (2007).

[5] W.-Y. Cha, T. Miki, Y. Sasaki, M. Hino, Temperature dependence of Ti Deoxidation Equilibria of Liquid Ironi in Coexistence with Ti_3O_5 and Ti_2O_3,ISIJ Intern. **48**, 729-738 (2008).

[6] D. Podorska, J. Wypartowicz, The optimisation of titanium and nitrogen concentration in micro-alloyed steel, Arch. Met. Materials **54**, 823-828 (2009).

[7] J. Iwanciw, D. Podorska, J. Wypartowicz, Zachowanie dodatków stopowych w procesie rafinacji pozapiecowej stali (Behavior of alloying elements in ladle refining of steel), Hutnik – Wiad. Hutn. **57**, 132-139 (2010).

[8] http://www.factsage.com

[9] J. Iwanciw, Simulator of Steelmaking Processes for Work in Real Time, Polska Metalurgia w latach 1998-2002, Komitet Metalurgii Polskiej Akademii Nauk **I**, 186-192.

Received: 10 February 2011.