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## MODELING OF OXIDE PRECIPITATES CHEMICAL COMPOSITION DURING STEEL DEOXIDIZATION

### MODELOWANIE SKŁADU CHEMICZNEGO WYDZIELEŃ TLENKOWYCH PODCZAS ODTLENIANIA STALI

The work analyses the possibilities of modeling the process of steel deoxidization from the view-point of thermodynamic equilibrium between liquid steel and oxide precipitates. Two calculation procedures were employed, which make use of WYK\_STAL authors' program and commercial software FactSage. Two kinds of steel were taken into account, one with considerable titanium addition and the second without titanium. The variation of chemical composition of non-metallic precipitates with titanium concentration, aluminum addition and temperature was determined. The apparent influence of assumed thermodynamic model on the composition of non-metallic precipitate was stated.

*Keywords:* simulation, deoxidization, steel, titanium, aluminum, nitrides

Praca analizuje możliwości modelowania procesu odtleniania stali w aspekcie równowagi termodynamicznej między ciekłą stalą a wydzieleniami tlenkowymi. Zastosowano dwie procedury obliczeniowe z wykorzystaniem komercyjnego pakietu FACTSage oraz własnego programu WYK\_STAL. Obliczenia wykonano dla dwóch gatunków stali, z których jedna posiada znaczny dodatek tytanu. Obliczono, jak zmienia się skład wydzieleni tlenkowych pod wpływem stężenia tytanu, dodatku glinu oraz temperatury. Stwierdzono wyraźny wpływ przyjętego modelu termodynamicznego procesu na uzyskany skład fazy niemetalicznej.

### 1. Introduction

Operations of ladle metallurgy are directed toward two main goals: setting of required concentration of basic components, including micro-additions, as well as maximal removal of components which deteriorate the quality of steel, as sulphur, phosphorus and mainly oxygen. The target level of oxygen should be always as low as possible. However, the level of nitrogen has to be set in some concentration range, corresponding to expected functions of nitrides in grain size and structure control. Removal of oxygen through oxide formations offers the variety of possibilities, even within one target composition of steel. Simultaneous action of manganese, silicon, and titanium or aluminum results in shift of thermodynamic equilibrium towards deeper deoxidization as well as in formation of liquid precipitates, which are more easily removed from steel.

The deoxidization process must be properly designed for particular kind of steel. This particularly regards the steel with titanium, which is also strong deoxidizer. Though the thermodynamic background of deox-

idization processes including basic parameters of phases description, as well as the computer software for equilibrium calculations are generally available, some important data are still lacking.

Recent work [1] analysed the interconnection between the simultaneous reactions of aluminum and titanium with dissolved oxygen and nitrogen. Present work is mainly focused on oxides formation, so two steels of low nitrogen content were considered, for which the formation of nitrides does not influence the quantitative relations between the oxides.

### 2. Mathematical programs employed in the simulation of processes of steel deoxidation

The quantitative thermodynamic analysis of oxide phase formation in steel in the course of its deoxidization consists of determination of subsequent states of equilibrium between liquid steel and non-metallic, mainly oxide phase, taking into account the amount of deoxidizing agents added and temperature variation. Two computer programs have been employed in the present study:

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- WYK\_STAL software, compiled by Iwanciw[ 2]
- FACTSage commercial software –[3]

WYK\_STAL program is assigned for the simulation of metallurgical processes, e.g. deoxidization on the basis of the parameters of thermodynamic equilibrium in the system in subsequent time steps. The simple thermodynamic model is employed in the program, in which the activities of liquid steel components are described by means of Wagner – Chipman equations [4]. The non-metallic phase, composed of oxides and sometimes nitrides mixture may be alternatively described as an ideal or regular solution.

The commercial FACTSage software (*Equilibrium* module) considers the equilibrium states in the system. Its application in simulation of deoxidizing operations is however possible, if subsequent equilibrium states during addition of deoxidizing agent are taken into account.

### 3. The steels subject to analysis of oxide precipitates formation in the present work

Deoxidization of two kinds of steel was simulated in the present work. They are shortly termed as “titanium steel” and “vanadium steel”. The typical composition of titanium steel is presented in Table I.

TABLE 1  
Chemical composition (% mas.) of titanium steel (18 HGT steel, according to Polish standard PN – 89/H – 84030/02.)

| C             | Mn            | Si            | P    | S    | Al | Ni | Cr        | Mo | V | Ti            |
|---------------|---------------|---------------|------|------|----|----|-----------|----|---|---------------|
| 0.16–<br>0.24 | 0.80–<br>1.10 | 0.17–<br>0.37 | 0.04 | 0.04 | –  | –  | 1.0 – 1.3 | –  | – | 0.08–<br>0.15 |

Table II presents the masses of components in the system subject to simulation. The starting oxygen concentration was set at the level 50 ppm, this of titanium at the level 0.15 mass % (1500 ppm). Aluminum addition to the system was equivalent to 40 – 200 ppm.

TABLE 2  
Mass of components of titanium steel (18 HGT) used as a starting point of simulation in the present work. (kg)

| Fe              | Mn                  | Si                  | O  | N  | Al       | C                   | Cr                  | Ti                  |
|-----------------|---------------------|---------------------|----|----|----------|---------------------|---------------------|---------------------|
| 10 <sup>6</sup> | 1.0·10 <sup>4</sup> | 2.5·10 <sup>3</sup> | 50 | 20 | 40 - 200 | 2.3·10 <sup>3</sup> | 1.3·10 <sup>4</sup> | 1.5·10 <sup>3</sup> |

Table III presents the chemical composition of vanadium steel. It should be noted, that chromium and vanadium present in this steel do not participate in deoxidization according to the thermodynamic conditions. Thus the formation of the oxides of iron, silicon, manganese and aluminum only takes place in the process.

TABLE 3  
Chemical composition of vanadium steel (15 HGF) according to producer’s standard (mass %)

| C             | Mn          | Si            | P    | S    | Al | Ni  | Cr          | Mo | V             | Ti |
|---------------|-------------|---------------|------|------|----|-----|-------------|----|---------------|----|
| 0.12–<br>0.17 | 1.0–<br>1.3 | 0.15–<br>0.35 | 0.04 | 0.04 | –  | 0.4 | 1.0–<br>1.3 | –  | 0.08–<br>0.12 | –  |

The mass of components of the system subject to simulations are presented in table IV. The starting oxygen concentration was set at the level 50 ppm. The variable aluminum addition was at the level 40 – 200 ppm.

TABLE 4  
Mass of components of titanium steel (18 HGT) used as a starting point of simulation In the present work. (kg)

| Fe              | Mn                  | Si                  | O  | N  | Al       | C                   | Cr                  | V                   | Ni                  |
|-----------------|---------------------|---------------------|----|----|----------|---------------------|---------------------|---------------------|---------------------|
| 10 <sup>6</sup> | 1.3·10 <sup>4</sup> | 3.5·10 <sup>3</sup> | 50 | 50 | 40 - 200 | 1.7·10 <sup>3</sup> | 1.3·10 <sup>3</sup> | 1.2·10 <sup>3</sup> | 4.2·10 <sup>3</sup> |

### 4. Refining procedure

At the point of tapping from converter the steel contains roughly 500 ppm of oxygen. First step of deoxidization with the use of Mn and Si in the form of ferroalloys results in considerable decrease of oxygen concentration. The value of 50 ppm was assumed in the present work as the starting point of second stage of deoxidization with the simultaneous use of aluminum and titanium (titanium steel) or aluminum only (vanadium steel). This may correspond to operation taking place in the ladle during argon blowing.

In the simulation in the present work the results of addition of variable amount of aluminum to the system was determined. The range considered was 40-200 ppm Al (with respect to total mass of the system). In the case of titanium steel it was assumed, that the whole amount of titanium – 0.15 mass % with respect to total mass of the system was introduced simultaneously with aluminum. The results obtained in previous simulation of AH-36 steel [1] have been taken for comparison. The concentration of titanium in AH-36 steel is much lower, and in the simulation two titanium levels: 167 ppm and 333 ppm were taken.

The simulation was carried out for two values of temperature: 1820 K – the average temperature of steel in the ladle during argon blowing, and 1790 K, which is the final temperature of steel deoxidization in ladle.

### 5. Results of simulations carried out by means of FactSage package

The results of simulations carried out by means of FactSage software regarding the composition of precip-

itates are presented in Figs 1-9. The dependence of precipitate composition (expressed as molar fraction) on aluminum addition at 1820 K is presented. The aluminum addition is expressed in ppm in relation to total initial mass of the system, prior to precipitation. This convention is valid within the whole publication. Figs. 1 and 2 demonstrate two modes of calculation for titanium steel (18HGT). In the first mode (Fig. 1) both titanium oxides  $Ti_2O_3$  and  $TiO_2$  are taken into consideration. In the second one (Fig. 2) only  $TiO_2$  oxide is assumed to exist. The difference between both modes is striking. In the first case (Fig. 1) titanium oxides evidently dominate at low aluminum addition. This is a result of high initial titanium concentration (0.15 mass %) in titanium steel (18HGT) as well as the thermodynamic data corresponding to Al – O and Ti – O interactions in steel. With increasing Al addition the concentration of  $Al_2O_3$  strongly increases, and at Al level equivalent to 200 ppm it exceeds the value of  $X_{Al_2O_3} = 0.6$ . If only the existence of  $TiO_2$  is allowed,  $Al_2O_3$  is the dominating component of oxide phase, as its contribution exceeds  $X_{Al_2O_3} = 0.5$  at as low Al addition as 60 ppm. It should be remarked that at Al addition 40 ppm no solution was obtained by means of FactSage program.

Fig. 3 presents the results obtained for vanadium steel (15HGF). The presence of vanadium does not influence the composition of precipitates, as the oxides of vanadium do not occur as the oxide phase components. It is clear, that in the absence of titanium, manganese and silicon play considerable role as steel deoxidizers. This role becomes weaker with increasing amount of aluminum added. The contributions of manganese and silicon oxides are similar, despite the fact, that manganese concentration in steel is 5 times higher.

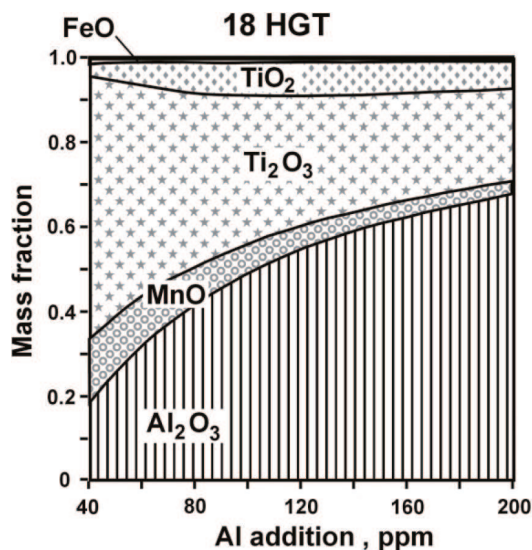


Fig. 1. The composition of oxide precipitates for titanium steel of initial titanium concentration 1500 ppm at the temperature 1820 K, calculated by means FactSage package. Titanium is assumed to exist both as  $Ti_2O_3$  and  $TiO_2$

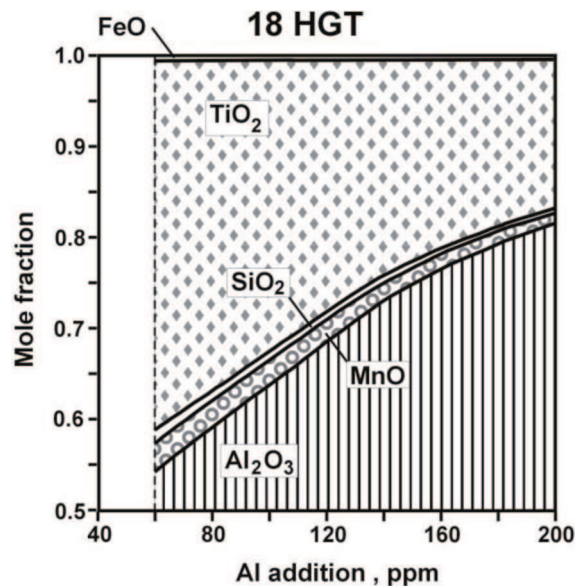


Fig. 2. The composition of oxide precipitates for titanium steel of initial titanium concentration 1500 ppm at the temperature 1820 K, calculated by means FactSage package. Titanium is assumed to exist as  $TiO_2$  only

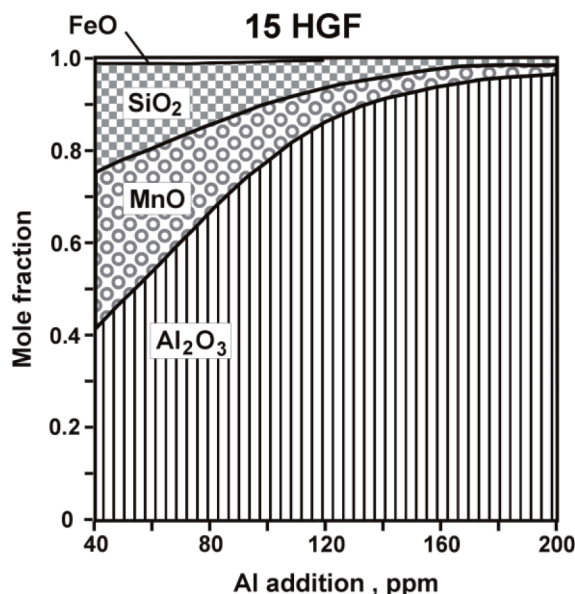


Fig. 3. The composition of oxide precipitates for vanadium steel, not containing titanium at the temperature 1820 K, calculated by means FactSage package

For comparison the results of calculations from [1] regarding the AH-36 steel are presented in analogous form (Figs. 4 and 5). The titanium concentrations in AH-36 steel is much lower in comparison to 18 HGT steel. Two titanium levels: 167 ppm and 333 ppm are considered. It may be noticed that  $Al_2O_3$  is the dominating component of the oxide phase even at the lowest Al addition, as its mole fraction exceeds 0.5. What regards titanium oxides,  $TiO_2$  is the predominant one at both titanium levels. The proportion between manganese and silicon oxides is very close to the proportion between

manganese and silicon. Quite different effect was observed in the case of 15HGF steel (without titanium). It seems, that in the presence of stronger deoxidizers the difference in deoxidizing power between silicon and manganese is less important.

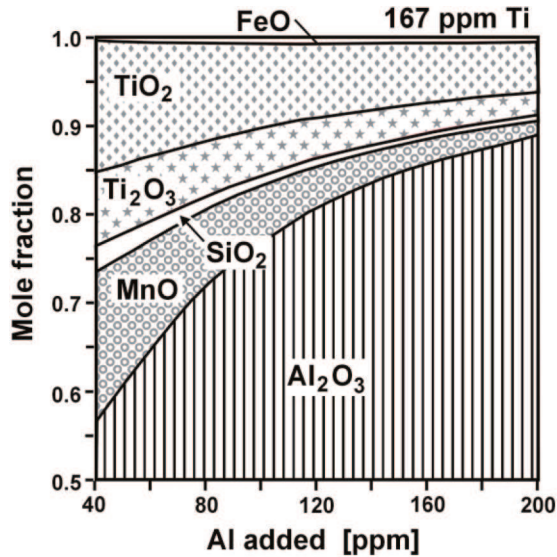


Fig. 4. The composition of oxide precipitates for AH-36 steel of initial titanium concentration 167 ppm at the temperature 1820 K, calculated by means FactSage package, based on the data of [1]

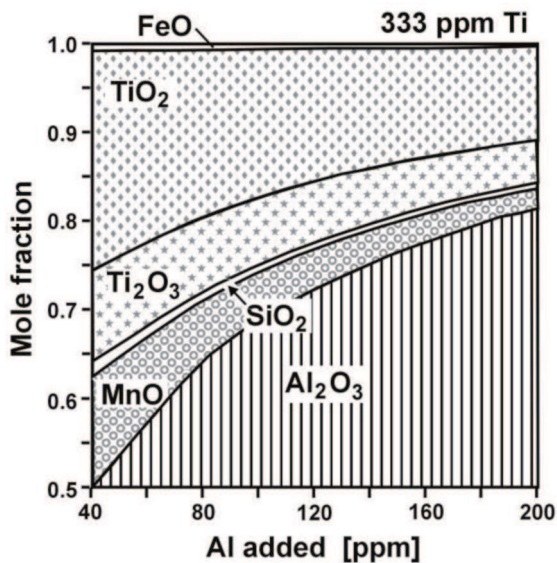


Fig. 5. The composition of oxide precipitates for AH-36 steel of initial titanium concentration 333 ppm at the temperature 1820 K, calculated by means FactSage package, based on the data of [1]

Figures 6 and 7 demonstrate the behavior of iron and manganese oxides in various steels. The figures are based on the results of calculations carried out by means FactSage software in [1] and these from the present work. It may be seen, that the molar concentrations of MnO are generally at least an order of magnitude higher than these of FeO. The highest concentration of FeO within

the calculation range was ca  $X_{FeO} = 0.01$ , while this of MnO was  $X_{MnO} = 0.3$ . This concentration considerably decreases with the amount of Al added. The curves presenting dependence of FeO concentration with increasing Al content in steel are very similar for various kinds of steel. The highest FeO concentration was obtained for 18HGT steel; this result is difficult to explain. The concentration of MnO was evidently highest for 15HGF steel, what results from the absence of titanium in this steel.

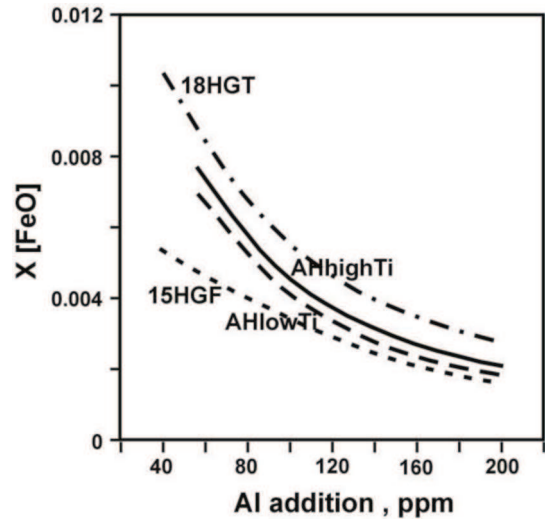


Fig. 6. Comparison of FeO concentration in oxide phase in the steels 18HGT, 15HGF and AH-36 (two levels of Ti) at 1820 K based on the results of FactSage calculations in [1] and in the present work

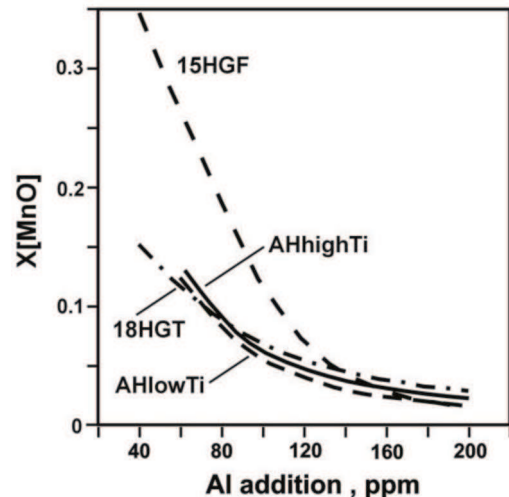


Fig. 7. Comparison of MnO concentration in oxide phase in the steels 18HGT, 15HGF and AH-36 (two levels of Ti) at 1820 K based on the results of FactSage calculations in [1] and in the present work

Fig 8 and 9 regard the concentration of aluminum and oxygen in various kinds of steel. Only a part of aluminum added as oxidizing agent is bonded with oxygen. From the shape of dependence between aluminum remained in steel and total aluminum added it may be

deduced, that the fraction of aluminum bonded in oxide phase is almost constant. The curves for various steels are very close to each other. However, the titanium (18HGT) steel shows the highest level of Al.

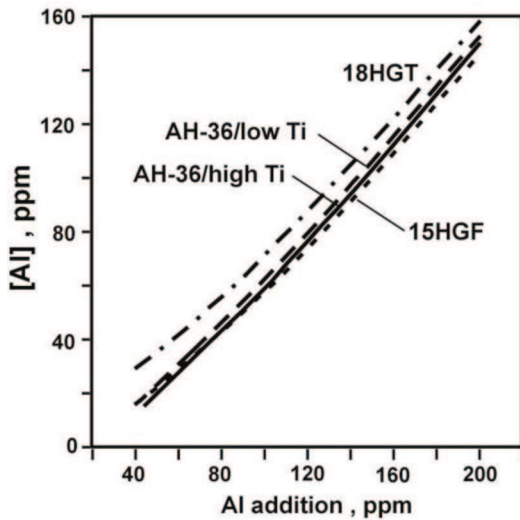


Fig. 8. Comparison of Al concentration in the steels 18HGT, 15HGF and AH-36 (two levels of Ti) at 1820 K based on the results of FactSage calculations in [1] and in the present work

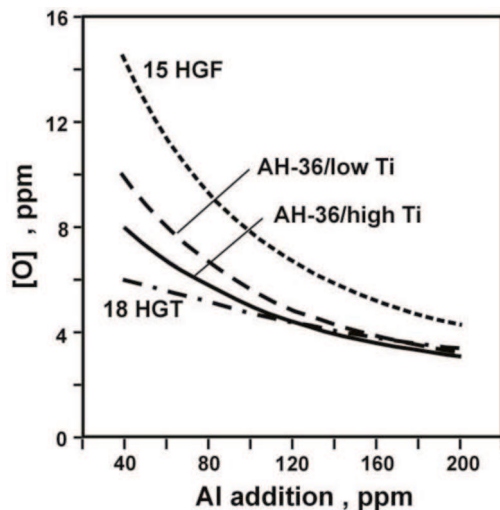


Fig. 9. Comparison of oxygen concentration in the steels 18HGT, 15HGF and AH-36 (two levels of Ti) at 1820 K based on the results of FactSage calculations in [1] and in the present work

## 6. Results of simulations carried out with the use of WYK\_STAL program

Figs. 10 and 11 present the results of simulations regarding titanium steel (18HGT) by means of WYK\_STAL program. Two values of temperature, 1820 K and 1790 K were taken into account. The oxide solution was assumed as the ideal one. It may be noticed that the influence of temperature on oxide phase composition

is not strong. Slightly higher  $\text{Al}_2\text{O}_3$  concentrations were obtained at 1790 K.

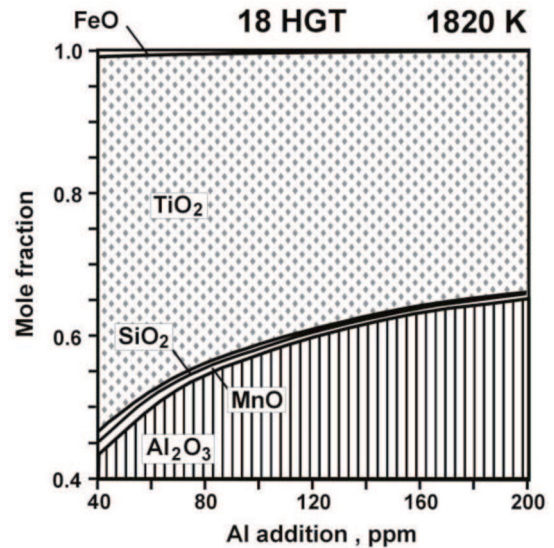


Fig. 10. The results of calculations of chemical composition of oxide precipitates in equilibrium with titanium (18 HGT) steel for the temperature 1820 K. obtained by means of WYK\_STAL software. Oxide phase is described as ideal solution

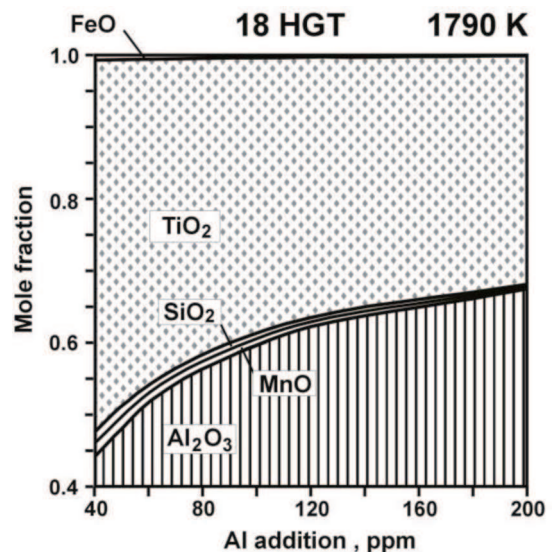


Fig. 11. The results of calculations of chemical composition of oxide precipitates in equilibrium with titanium (18 HGT) steel for the temperature 1790 K. obtained by means of WYK\_STAL software. Oxide phase is described as ideal solution

The results of calculations for the titanium steel (18HGT) based on the regular solution model of oxides are not presented here. They show weak influence of aluminum addition on  $\text{Al}_2\text{O}_3$  content in liquid phase, which seem unrealistic. The wrong values of interaction parameters in oxide phase seem to be the probable reason.

The results obtained for vanadium steel (15HGF) are presented in in Figs. 12-15. Figs 12 and 13 were obtained

under assumption of ideal oxide solution. In this case the  $\text{Al}_2\text{O}_3$  concentration in oxide phase was very high. Even at low amounts of introduced aluminum, the concentration of  $\text{Al}_2\text{O}_3$  exceeded the value  $X_{\text{Al}_2\text{O}_3} = 0.8$ . At higher amounts of added aluminum, e.g. 200 ppm the oxide concentration approaches  $X_{\text{Al}_2\text{O}_3} = 0.97$ . The proportion between manganese and silicon oxide amounts varies with the amount of added aluminum. At low aluminum additions silicon oxide predominates, while at higher aluminum additions the manganese oxide concentration is higher than that of silicon oxide. The concentration of iron oxide is generally lower than  $X_{\text{FeO}} = 0.01$ .

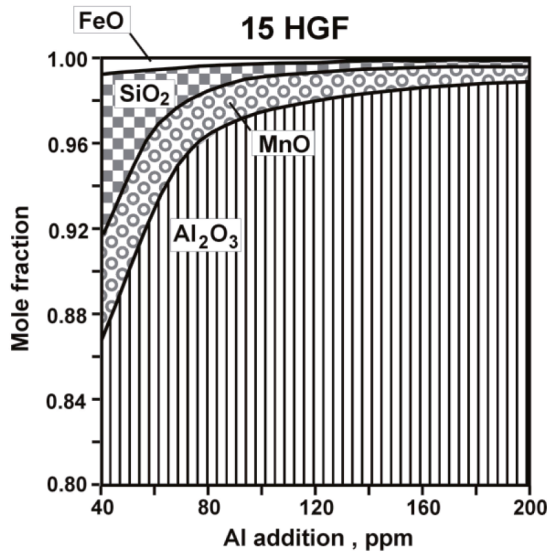


Fig. 12. The results of calculations of chemical composition of oxide precipitates in equilibrium with vanadium (15HGF) steel for the temperature 1820 K. obtained by means of WYK\_STAL software. Oxide phase described as an ideal solution

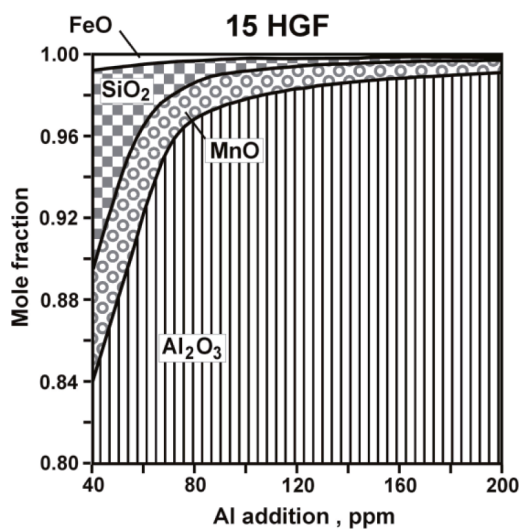


Fig. 13. The results of calculations of chemical composition of oxide precipitates in equilibrium with vanadium (15 HGF) steel for the temperature 1790 K. obtained by means of WYK\_STAL software. Oxide phase described as ideal solution

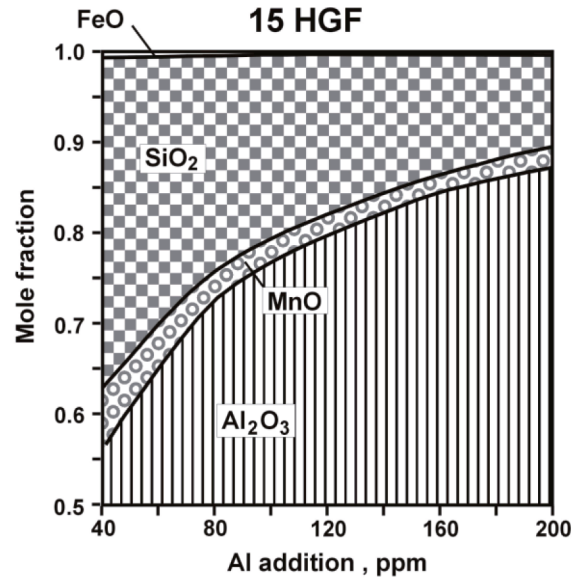


Fig. 14. The results of calculations of chemical composition of oxide precipitates in equilibrium with vanadium (15HGF) steel for the temperature 1820 K. obtained by means of WYK\_STAL software. Oxide phase described as the regular solution

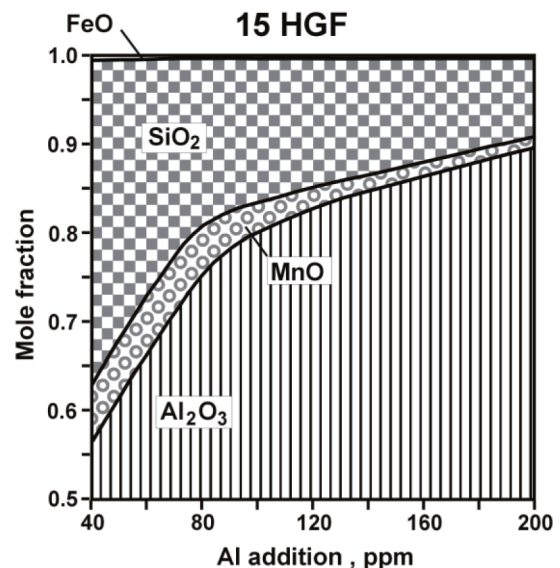


Fig. 15. The results of calculations of chemical composition of oxide precipitates in equilibrium with vanadium (15 HGF) steel for the temperature 1790 K. obtained by means of WYK\_STAL software. Oxide phase described as the regular solution

Quite different compositions of oxide phase is obtained, if regular solution model is employed in thermodynamic description of this phase. It follows from the Figs 14 and 15, that in this case the  $\text{Al}_2\text{O}_3$  concentration varies within the range  $X_{\text{Al}_2\text{O}_3} = 0.55$  to 0.85. In these circumstances the composition of  $\text{SiO}_2$  becomes evidently higher than this of  $\text{MnO}$ . The influence of temperature on the composition of oxide phase is small. The decrease of temperature from 1820 to 1790 K results in only slight increase in  $\text{Al}_2\text{O}_3$  concentration. What regards  $\text{MnO}$ , the decrease of temperature results in small increase of  $\text{MnO}$

concentration at small additions of Al, and small decrease in MnO concentration at higher amounts of Al.

## 7. Conclusions

The simulations carried out in the present work were focused on explanation of the relation between steel initial composition, amount of added deoxidizer and resulting composition of non-metallic precipitates. The simulation was carried out by means of two computer programs, which determine the parameters of thermodynamic equilibrium at subsequent steps of the process. It was proved that simple program WYK\_STAL yields valuable results, in many aspects corresponding to those obtained by means of commercial software. It was stated that deoxidization of steel containing titanium results in formation of complex oxides of titanium and aluminum, with small contribution of manganese and silicon oxide and with minor amount of iron oxide. If steel does not contain titanium, the contributions of silicon and manganese oxides are substantial.

At nitrogen level of the order 50 ppm the formation of nitrides must be considered in simulation. The form of nitrides (as the component of non-metallic solution or as a pure substance) is decisive for its amount produced in reaction with titanium or aluminum. Incomplete databases resulting from the shortage of experimental data make impossible the definite solution to this problem. Titanium affinity to nitrogen is higher than this of aluminum, thus in the case of titanium containing steel the formation of nitrides must be taken into account.

Another important factor influencing the composition of non-metallic phase formed during deoxidization is the stoichiometry of titanium oxides. As the thermodynamic stability of oxides  $Ti_2O_3$ ,  $Ti_3O_5$  and  $TiO_2$  considerably depends on the oxygen activity in liquid steel, during the course of deoxidization the kind of existing titanium oxide varies.

Both above factors cooperate with one another, i.e. formation of nitrides varies the behavior of oxides and vice versa. Thus the proper calculation of equilibrium state parameters between liquid steel and non-metallic precipitates is up to now hardly possible.

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