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#### EVOLUTION OF EQUILIBRIUM COMPOSITION OF MnO-SiO<sub>2</sub> AND Al<sub>2</sub>O<sub>3</sub>-MnO-SiO<sub>2</sub> INCLUSIONS IN LIQUID Fe AND Fe-36%Ni ALLOY DURING COOLING

#### EWOLUCJA RÓWNOWAGOWEGO SKŁADU CIEKŁYCH WTRĄCEŃ MnO-SiO<sub>2</sub> ORAZ Al<sub>2</sub>O<sub>3</sub>-MnO-SiO<sub>2</sub> W STOPIE Fe-36%Ni ORAZ W CIEKŁYM Fe W CZASIE CHŁODZENIA

Evolution of chemical composition of inclusions for Fe-36%Ni melt on cooling was simulated on the basis of theoretical analysis. The equilibrium states for deoxidization reactions using manganese, silicon and aluminum were found by using the subregular solution thermodynamic model, including the interaction parameters and the activity coefficients for O, Mn, Si i Al at infinite dilution in iron and nickel. The equilibrium compositions of the inclusions when cooling the melt were computed for Fe-36%Ni for the temperatures from 1873K to 1773K. For comparison, the same analysis was made for pure iron melt. The obtained results indicate different behavior of the inclusions for those melts. For Fe-36%Ni, either MnO-SiO<sub>2</sub> inclusions or Al<sub>2</sub>O<sub>3</sub>-MnO-SiO<sub>2</sub> ones always increase substantially in MnO content on cooling. When Al<sub>2</sub>O<sub>3</sub> content goes up, the effect gets weaker. As to the pure iron melt, the inclusions behave more differently, i.e., the MnO content may go up, go down or stay constant depending on the initial inclusion composition. Despite of the fact that Al<sub>2</sub>O<sub>3</sub>-MnO-SiO<sub>2</sub> inclusions fluctuate significantly as to their compositions for Fe-36%Ni melt, it seems however, that it would be easier for this melt - in comparison to pure iron one - to forecast such a chemical target composition which would allow to achieve the desired composition of the inclusions left within the residual melt after metal cooling from 1873K to 1773 K.

Keywords: Fe-Ni melt, deoxidization, liquid inclusions, cooling, thermodynamics

Przeprowadzono teoretyczną symulację zmiany składu wtrąceń w stopie Fe-36%Ni podczas chłodzenia. Stałe równowagi reakcji odtleniania manganem, krzemem i glinem obliczono zakładając model subregularny i wykorzystując parametry oddziaływania oraz współczynniki aktywności O, Mn, Si i Al w nieskończonym rozcieńczeniu w żelazie i niklu. Obliczono równowagowe składy wtrąceń w procesie chłodzenia Fe-36%Ni od 1873K do 1773K. Porównawczo wykonano taką samą analizę dla żelaza. Uzyskane wyniki wskazują, że wtrącenia zachowują się różnie w obu metalach. W stopie Fe-36%Ni, zarówno wtrącenia MnO-SiO<sub>2</sub> jak i Al<sub>2</sub>O<sub>3</sub>-MnO-SiO<sub>2</sub> zawsze wzbogacają się w znacznym stopniu w MnO gdy temperatura spada. Zwiększenie zawartości Al<sub>2</sub>O<sub>3</sub> osłabia ten efekt. Wtrącenia w żelazie zachowują się bardziej różnorodnie – ułamek molowy MnO może zwiększać się, zmniejszać lub pozostawać stały, zależnie od początkowego składu wtrącenia. Mimo, że wtrącenia Al<sub>2</sub>O<sub>3</sub>-MnO-SiO<sub>2</sub> ulegają znacznym zmianom w stopie Fe-36%Ni, to wydaje się, że prognozowanie takiego składu wtrąceń w 1873K aby po ochłodzeniu metalu i wypłynięciu części z nich, pozostałe wtrącenia miały pożądany skład, może być łatwiejsze w Fe-36%Ni niż w żelazie.

#### 1. Introduction

The aim of this study was the estimation of control measures for chemical compositions of such oxide inclusions like Al<sub>2</sub>O<sub>3</sub>-MnO-SiO<sub>2</sub> by cooling Fe-36%Ni melt and then making a comparison of the found data to the ones for the pure Fe melt. The Fe-36%Ni alloy, called invar, is specific in an extremely low thermal expansion coefficient, so it is applied, among the others, for the elements which must exhibit constant dimensions within broad temperature variations. Invar is used mainly as

the material for high technologies. That kind of material must exhibit not only a very low oxygen content, but also the inclusions entrapped within the solidified melt bulk after solidification should have a strictly controlled composition. In order to achieve that goal one has to control carefully the inclusions behavior during alloy refining and solidification. Unfortunately, the experimental investigations on deoxidization processes for Fe-Ni melts are being run seldom and only for selected nickel contents and temperatures. Therefore, some theoretical approach is needed. The experimental investigations and

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theoretical simulations executed so far point out that Mn and Si are stronger deoxidizers when used for Fe-Ni melts than for pure Fe, and their effectiveness grows with nickel content in the metal melt [1-4]. Aluminum exhibits the opposite behavior. For Fe-Ni melt, it is weaker as deoxidizer when compared to its deoxidizing power for pure iron melt [5,6]. However, this feature does not change proportionally to increasing Ni content. For pure Ni melt, Al deoxidizes with almost the same effectiveness like for pure Fe melt, while it exhibits the weakest deoxidizing potential for the melts of about 40-50%Ni, depending on temperature. Oxide inclusions which are formed by cooling ought to be fluid as long as possible along the falling temperature to secure satisfactory final cleanness of the alloy. To estimate the temperature effect on the inclusions' composition one needs to know the temperature dependence of the deoxidization reaction equilibrium constants. Those have to be estimated theoretically as there is no enough experimental data. The sub-regular model was used in the present work to set the equilibrium constants required for calculation of chemical compositions of inclusions.

As to the compositions of the inclusions left in the metal alloy after cooling process, they are affected by many factors. When solely the deduced equilibrium constants are used for composition/temperature estimates for the oxide inclusions, the obtained results are of an approximate value only. The reason is that a substantial part of the inclusions escapes the metal by float-out movement so the inclusions left within the metal bulk become the very substance affected by decreasing temperature. Therefore, it is not feasible at the moment to achieve any desired composition of the inclusions after solidification of the melt by using the data computed for 1873K only. However, it is important to know, how temperature affects the evolution of chemical composition of oxide inclusions with no regard of floating-out process. Such computations will be presented in this study for Fe-36%Ni melt.

#### 2. Description of calculation model

The formulae, input data and output data used in the calculation procedure are presented below.

# a) First-order interaction parameters $\varepsilon_i^j$ and $e_i^j$ in Ni, Fe and Fe-36%Ni at 1873K

The interaction parameters,  $\varepsilon_{i(\text{Fe})}^{j}$ ,  $\varepsilon_{i(\text{Ni})}^{j}$ , based on the mole fractions for dissolved species "i", "j" being oxygen, manganese, silicon and aluminum were calculated from Wagner's interaction coefficients  $e_{i(\text{Fe})}^{j}$  and  $e_{i(\text{Ni})}^{j}$  according to the equation, where *M* is the atomic mass and Me denotes Fe or Ni

$$\varepsilon_{i(Me)}^{j} = (230M_{j}/M_{Me}) \cdot e_{i(Me)}^{j} + (M_{Me} - M_{j})/M_{Me},$$
 (1)

The interaction parameters,  $\varepsilon_{i(\text{Fe-Ni})}^{j}$ , in Fe-36%Ni were calculated from the approximation

$$\varepsilon_{i(\text{Fe-Ni})}^{j} = X_{Fe} \varepsilon_{i(\text{Fe})}^{j} + X_{\text{Ni}} \varepsilon_{i(\text{Ni})}^{j}, \qquad (2)$$

where X denotes the mole fraction, and then  $\varepsilon_{i(\text{Fe-Ni})}^{J}$ were converted to  $e_{i(\text{Fe-Ni})}^{j}$  using the equation (1) where symbol Me denotes Fe-36% alloy and the atomic mass of that alloy equals

$$M_{\rm (Fe-Ni)} = X_{Fe}M_{\rm (Fe)} + X_{\rm Ni}M_{\rm (Ni)}.$$
 (3)

TABLE 1

The calculated values of  $e_i^{\rm J}$  in Fe-36%Ni for *i* and *j* as O, Mn, Si, Al and C are presented in Table 1 along with the ones used in iron [7-10] and nickel [1,2,11-13] as the input data. Because the interaction parameters in nickel are known only for few elements, one can not calculate all the parameters in Fe-36%Ni, as it is seen in Table 1. In that case, the data for iron will be applied directly to Fe-36%Ni.

Metal		Fe	e		Fe-36%Ni				Ni			
i	0	Mn	Si	Al	0	Mn	Si	Al	0	Mn	Si	Al
$e_i^{O}$	-0.174	-0.082	-0.119	-1.979	-0.116	-0.571	-0.116	-2.150	0	-1.53	-0.110	-2.488
$e_i^{\mathrm{Mn}}$	-0.021	7.2.10-5	-0.015	0.035	-0.166	0.002	_	0.034	-0.450	0.006	_	0.031
$e_i^{\rm Si}$	-0.066	-0.033	0.103	0.056	-0.066	-	0.132	-	-0.065	-	0.190	_
$e_i^{\mathrm{Al}}$	-1.170	0.067	0.058	0.017	-1.272	0.064	-	0.040	-1.480	0.058	-	0.085
$e_i^{\rm C}$	-0.428	-0.054	0.18	0.091	-0.476	_	_	_	-5.70	_	_	_

First-order interaction parameters  $e_i^j$  calculated for Fe-36%Ni at 1873 K in comparison with these for Fe [7-10] and Ni [1,2,11-13]

# b) Activity coefficients of oxygen, manganese, silicon and aluminum at an infinite dilution in Fe-36%Ni alloy, $\gamma_{i(\text{Fe}-\text{Ni})}^{o}$ , at 1873 K

Activity coefficients in Fe–36%Ni alloy,  $\gamma^{o}_{i(\text{Fe-Ni})}$ , were estimated on the basis of the data for iron and nickel dilute solutions,  $\gamma^{o}_{i\text{Fe}}$ ,  $\gamma^{o}_{i\text{Ni}}$  (the review and details are presented in [14]) and the formula coming from the sub-regular solution model [15]:

$$\ln \gamma_{i(\text{Fe}-\text{Ni})}^{o} = X_{\text{Fe}} \ln \gamma_{i(\text{Fe})}^{o} + X_{\text{Ni}} \ln \gamma_{i(\text{Ni})}^{o} + X_{\text{Fe}} X_{\text{Ni}} [X_{\text{Ni}} (\ln \gamma_{i(\text{Ni})}^{o})$$
$$- \ln \gamma_{i(\text{Fe})}^{o} + \varepsilon_{i(\text{Ni})}^{\text{Fe}}) + X_{\text{Fe}} (\ln \gamma_{i(\text{Fe})}^{o} - \ln \gamma_{i(\text{Ni})}^{o} + \varepsilon_{i(\text{Fe})}^{\text{Ni}})]$$
(4)

The parameters  $\varepsilon_{i(\text{Fe})}^{\text{Ni}}, \varepsilon_{i(\text{Ni})}^{\text{Fe}}$ , used in the equation (4) are presented in [14].

# c) Temperature dependence of Mn, Si, Al – deoxidization equilibrium constants in Fe-36%Ni

Starting from the standard Gibbs energies of the MnO, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> formation reactions, and using the activity coefficients of O, Mn, Si and Al at an infinite dilution in Fe–36%Ni, the equilibrium constants, K, of the deoxidization reactions were calculated [16]. To assure the consistency of input data, the same procedure was applied to the deoxidization equilibria in iron, instead of using the recommended values [16]. The formulae and the values at 1873K and 1773K are presented in Table 2.

It is to be noted that in the available literature there have been not found temperature dependences of the equilibrium constants for the deoxidizers considered in this study over the temperature range 1773K-1873K. For Fe-36%Ni melts only few data for the equilibrium constants may be found [3,5,6,17,18] and they usually refer only to one definite temperature.

 TABLE 2

 Equilibrium constants of deoxidization reactions in liquid Fe and

 Fe-36%Ni at 1873K-1773K temperature range used in this study

Reactions	Equilibrium constants, log K						
Treactions	Fe	Fe-36Ni					
[Mn] + [O] = (MnO)	14481/T – 6.457	15301/T – 6.723					
$[Si] + 2[O] = (SiO_2)$	31029/T - 11.912	27427/T – 9.752					
$2[Al] + 3[O] = (Al_2O_3)$	61390/T – 19.119	52434/T – 15.676					

## d) Activities of oxide components of inclusions

The chemical activities of  $Al_2O_3$ , MnO and  $SiO_2$  oxides in liquid MnO-SiO<sub>2</sub> and  $Al_2O_3$ -MnO-SiO<sub>2</sub> solutions as the function of the composition of inclusion and the temperature within the range of 1873K-1773K were calculated by means of FactSage<sup>TM</sup>package data. The details of calculation procedure are given in [16].

# e) Evolution of liquid inclusions composition in equilibrium with Fe-36%Ni and Fe melts during the temperature drop from 1873K to 1773K

Starting from the given metal compositions, the compositions of the inclusions formed at 1873K were calculated from the equilibrium constants,  $K_{R_xO_y}$ , of de-oxidization reactions

$$K_{R_xO_y} = \frac{a_{R_xO_y}}{([\mathscr{M}R] \cdot f_R)^x \cdot ([\mathscr{M}O] \cdot f_O)^y}$$
(5)

where:

R – deoxidizing element (Mn, Si, Al),

 $a_{R_xO_y}$  – activity of  $R_xO_y$  oxide in liquid inclusion,

[%R], [%O] – mass % concentration of element R and oxygen dissolved in metal,

 $f_R$ ,  $f_O$  – Henrian activity coefficient of R and O dissolved in metal.

The activity coefficients of MnO and SiO<sub>2</sub> in liquid MnO-SiO<sub>2</sub> inclusions or MnO, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> in liquid Al<sub>2</sub>O<sub>3</sub>-MnO-SiO<sub>2</sub> inclusions are the functions of inclusion compositions (the mole fractions). The activity coefficients of R and O dissolved in metal melts,  $f_R$ ,  $f_O$ , are the functions of concentration (mass %). Distribution of Mn, Si, Al and O elements between metal and inclusion must obey the boundary condition being the mass balance of that element.

The author's own program [16] was employed, in which the equilibrium parameters in two-phase system metal – oxide solution was determined. The solution required the equal values of oxygen activity for the deoxidization reactions involving Mn, Si and Al.

The compositional variation of inclusions through the temperature falling by 100 degree till 1773K with the step of 10K was calculated by the same procedure.

# 3. Comparison of the experimental data with calculated deoxidization equilibrium constants for Fe-36%Ni

The authors made a comparison of the equilibrium relationships for the deoxidizer and the oxygen contents resulting from the equations presented in Table 2 with those reported in the literature. It is presented in Fig. 1a (Si) and b (Al). The comparison was limited to the concentration regions which are close to the ones considered in the sections following below. The computation results from Tab. 2 are presented for two temperatures: 1873K (full line) and 1773K (dotted line). The experimental data refer to Fe-Ni melt with  $30\% \div 40\%$ Ni content within the temperature region 1773K -1923K.

For manganese there is only one experimental result reported at 1773K for Fe-36%Ni [3]. It fits the computation result. Other experiments at 1873K [13] were run



Fig. 1. Relationship between concentrations of oxygen and silicon (a) or aluminum (b) dissolved in Fe-36%Ni melt for 1873K (full lines) and 1773K (dotted lines)

0

-3.5

b)

in a crucible containing Al<sub>2</sub>O<sub>3</sub>, thus oxide phase of MnO contained small amounts of Al<sub>2</sub>O<sub>3</sub>, which may effect in a substantial drop of the equilibrium contents of dissolved oxygen in Fe-Ni melt.

-1.2

-0.8

log Si / mass %

-0.4

-1.6

a)

The experimental data for silicon in Fig.1a refer to Fe-35%Ni [4] for 1873K and 1923K, and to Fe-40%Ni [13] for 1873K and 1823K. For 1773K there is no experimental data. Additionally, there is presented one point for Fe-36%Ni calculated on the basis of Darken's quadratic formalism [18]. The results for Fe-35%Ni and Fe-36%Ni at 1873K fit quite well the calculated curve. The experimental results for Fe-40%Ni at 1873K are below the curve for Fe-36%Ni. From theoretical analysis of the equilibrium constants for deoxidization of Fe-Ni melt of different nickel contents using silicon as deoxidizer one can deduce that silicon is more effective in Fe-Ni melt than in pure Fe. This feature becomes gradually more apparent when nickel content goes up. So, the experimental data for Fe-40%Ni melt should be located below the curve for Fe-36%Ni as one can see for 1873K in Fig. 1a.

The calculated effect of aluminum deoxidization was compared in Fig. 1b to experimental data for Fe-30%Ni [6] and Fe-40%Ni [5,13,17] at 1873K. There is no data for Fe-36%Ni. The performed computations of the oxygen level using the equilibrium constants for Al-deoxidization in Fe-Ni melt with different nickel content point out that Al-deoxidization power in Fe-Ni melt is lower than in either pure iron or nickel and approaches minimum for ca. 40-50%Ni, depending on temperature. It means that the experimental data for Fe-36%Ni should be slightly below the ones for Fe-40%Ni. It becomes apparent that the proposed theoretical graph for 1873K in Fig. 1b agrees fairly well with experiment.

log Al / mass %

-1.5

-0.5

-2.5

# 4. Composition variation of MnO-SiO<sub>2</sub> inclusions during cooling

The results of Al and Si deoxidization of Fe-36%Ni melt were compared to that of pure Fe when cooling from 1873K to 1773K. MnO-SiO<sub>2</sub> inclusions were liquid for the whole temperature region. At the initial temperature point of 1873K, the same composition of the inclusions was taken for either metal. Four variants of the compositions of the inclusions were considered. The total content of O, Si and C was identical for either metal for all the inclusions' variants being equal to:  $O_{tot.} = 0.04 \text{ mass}\%$ ; Si<sub>tot.</sub> = 0.12 mass%; C<sub>tot.</sub> = 0.3 mass%. Mn-contents were differentiated to secure adequate inclusions' compositions, which is set in Table 3.

TABLE 3

Total contents of Mn in Fe and Fe-36%Ni corresponding to inclusions of given mole fractions at 1873 K

No	Xuo	Mn [mass%]					
110	<sup>1</sup> MnO	Fe	Fe-36%Ni				
1	0.533	1.08	0.978				
2	0.515	0.908	0.821				
3	0.496	0.76	0.688				
4	0.472	0.62	0.563				

The equilibrium compositions of inclusions were computed for inclusions' growth by metal cooling from 1873K to 1773K. In Fig. 2, the evolution of inclusions' compositions is presented for every 10K step from 1873K to 1773K for Fe-36%Ni and pure Fe. The plots are denoted as follows: full lines with filled markers refer to steel, dotted lines with empty markers refer to Fe-Ni melt. The numbers 1, 2, 3, 4 correspond to the inclusions' variants.



Fig. 2. Compositional change of MnO-SiO<sub>2</sub> inclusions when cooling iron and Fe-36%Ni alloy from 1873K to 1773K

One can see a basic difference as to the inclusions behaviour in Fe-36%Ni alloy compared to the same inclusions in pure Fe. When cooling the inclusions in Fe-36%Ni they always get enriched in MnO with this effect being larger the lower is initial MnO content. Inclusions in Fe keep almost constant composition by cooling; the composition changes are minimal either in the direction of MnO increase or its drop. It means that to achieve any desired final composition of inclusion after cooling is more difficult for Fe-Ni melts compared to either Fe or steel.

In Fig. 3 there are presented the evolutions of equilibrium content of manganese and of oxygen dissolved in Fe-36%Ni (a) compared to Fe (b) by cooling. For 1873K, for each variant of the inclusions composition, the dissolved oxygen level is lower in Fe-36%Ni alloy than in Fe. The differences of the equilibrium oxygen contents between particular variants are lower for invar than for Fe while they are growing up by increasing temperature. Thus, by the variant inclusions No 1 and 4 the difference at 1873K is 5 ppm while at 1773K it drops down to 3 ppm for Fe-36%Ni. For pure Fe melt, the differences are 26.7 ppm and 10 ppm, respectively.

When it comes to a real deoxidization process, the formed inclusions posses differentiated composition due to non-uniform distribution of the deoxidizing agent in metal phase. The data of present authors may suggest that if such inclusions are formed in Fe-36%Ni, they should be less subject to homogenization of their compositions.



Fig. 3. Manganese and oxygen concentrations in steel (a) and Fe-36%Ni (b) in equilibrium with MnO-SiO<sub>2</sub> inclusions when cooling from 1873K to 1773K

No	Mn [mass%]		Si [mass%]		Al [ppm]		O <sub>tot</sub> [ppm]		X <sub>MnO</sub>		X <sub>SiO2</sub>		X <sub>Al<sub>2</sub>O<sub>3</sub></sub>	
	Fe	Alloy	Fe	Alloy	Fe	Alloy	Fe	Alloy	Fe	Alloy	Fe	Alloy	Fe	Alloy
1	0.55	0.517	0.22	0.236	58	59	400	390	0.392		0.513		0.095	
2	0.85	0.813	0.16	0.176	60	62	400	390	0.456		0.450		0.094	
3	0.7	0.667	0.05	0.054	78	82.5	4	550	0.500		0.406		0.094	
4	0.9	0.841	0.03	0.031	78	80	4	550		0.543 0.360		.360	0.097	
5	0.5	0.444	0.13	0.125	115	123	400	390	0.403		0.406		0.191	
6	0.7	0.488	0.1	0.062	90	92.6	300		0.433 0.359		.359	0.208		
7	0.9	0.75	0.05	0.043	90	96.6	300		0.470		0.315		0.215	
8	0.88	0.816	0.18	0.184	110	115	400 390		0.510		0.282		0.208	

Total contents of Mn, Si, Al, O in Fe and Fe-36%Ni corresponding to inclusions of given mole fractions at 1873 K

## 5. Compositional behaviour of Al<sub>2</sub>O<sub>3</sub>-MnO-SiO<sub>2</sub> inclusions during cooling

Eight compositions of  $Al_2O_3$ -MnO-SiO<sub>2</sub> inclusions, which at 1873K are in equilibrium with the elements dissolved in Fe-36%Ni and in Fe were taken into considerations. For 4 of those inclusions the mole fraction of  $Al_2O_3$  was about 0.1, while for the others – about 0.2. The mole ratio of MnO was within the range 0.4-0.5, while for SiO<sub>2</sub> within 0.3-0.5. The initial inclusions in Fe and Fe-36%Ni had the same compositions at 1873K. To fulfill this requirements the total contents of deoxidizers were suitably differentiated in both metals. The oxygen contents were taken for computations at a fairly high level in order to get more remarkable alterations of inclusions' compositions by cooling. The total contents of O, Mn, Si and Al in the melts ensuring formation of each inclusion in question is presented in Table 4. The carbon content was 0.1 mass%. The total oxygen for a given inclusion was kept at the same level or close to it in either metal melt being equal to 300ppm, 550ppm and ca. 400ppm.

The changes of the inclusions' compositions by decreasing temperature at equilibrium conditions down to 1773K were computed. The inclusions for the all temperature region stayed liquid. The compositional trajectories for Fe and Fe-36%Ni by decreasing temperature with a 25K step are presented in Fig. 4.



Fig. 4. Calculated trajectories of Al<sub>2</sub>O<sub>3</sub>-MnO-SiO<sub>2</sub> inclusions compositions in equilibrium with iron (filled markers) and Fe-36%Ni (empty markers) during cooling from 1873K to 1773K

The main difference between those two metal melts is that all inclusions in Fe-36%Ni (empty markers) grow rich significantly in MnO when temperature goes down. However, for Fe (filled markers), the inclusions get rich in MnO or in SiO<sub>2</sub>, depending on the initial chemical composition at 1873K. The other difference is that the Al<sub>2</sub>O<sub>3</sub> mole fraction affects more distinctly the inclusions' behaviour in Fe-36%Ni compared to Fe. The lower is the Al<sub>2</sub>O<sub>3</sub> mole fraction, the higher is MnO increase for inclusions in Fe-36%Ni.

By decreasing temperature, all the inclusions exhibited the  $Al_2O_3$  mole fraction drop. It is due to the fact that after formation of inclusions at 1873K, the amount of aluminum dissolved in melt is very low (0.1 - 2 ppm), thus – when cooling – only slight mass increase of  $Al_2O_3$  in inclusion may take place.

To sum up, inclusions in Fe-36%Ni change distinctly their composition,  $x_{MnO}$  always goes up, but when Al<sub>2</sub>O<sub>3</sub> is present, the effect becomes weaker. The ratios of MnO to SiO<sub>2</sub> for inclusions in Fe are lower, but the changes are fairly differentiated. One may conclude that any prediction of the initial composition in order to guess right the target composition of the inclusions should be easier for Fe-36%Ni. The composition of the inclusions left in the metal after cooling results not only from the trajectories presented in Fig.4, but also from the process of inclusions' floating-out. Therefore, the real inclusions' compositions left in metal would differ, nevertheless the computed data of this study may be of help for prediction of inclusions' compositions.

#### 6. Conclusions

The performed theoretical analysis of variation of inclusions' compositions during metal cooling points out that the inclusions behave differently in Fe-36%Ni when compared to pure Fe. The analysis was carried out for MnO-SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>-MnO-SiO<sub>2</sub> inclusions of various compositions.

The performed analysis of inclusions' compositions relates to the temperature drop from 1873K to 1773K. It points out that by cooling the metals:

- 1. the inclusions of the same initial composition change their composition differently for Fe-36%Ni compared to Fe. MnO-SiO<sub>2</sub> inclusions grow rich in MnO substantially when they are formed in Fe-36%Ni, while in Fe, the level of  $X_{MnO}$  is almost fixed with only small fluctuations
- 2. the investigated  $Al_2O_3$ -MnO-SiO<sub>2</sub> inclusions in Fe-36%Ni grow rich in the mole fraction of MnO,

however the presence of  $Al_2O_3$  makes this increase weaker (such results were found for a wide composition range of inclusions [16],

when considering the same Al<sub>2</sub>O<sub>3</sub>-MnO-SiO<sub>2</sub> inclusions in Fe, they exhibit different alterations of MnO mole fraction.

Therefore, one may conclude that any prediction of  $Al_2O_3$ -MnO-SiO<sub>2</sub> inclusions' compositions in Fe-36%Ni should be easier than in Fe as, firstly, the direction of the compositional changes is identical for the all inclusions and, secondly, those changes are distinctly weaker by presence of  $Al_2O_3$  in inclusion.

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