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ACTIVITY COEFFICIENTS OF MANGANESE, SILICON AND ALUMINUM IN IRON, NICKEL AND Fe-Ni ALLOYS

WSPÓŁCZYNNIKI AKTYWNOŚCI MANGANU, KRZEMU ORAZ GLINU W ŻELAZIE, NIKLU I STOPACH Fe-Ni

The effect of the nickel contents in Fe-Ni melts on the activity coefficients of oxygen and such deoxidisers as manganese, silicon and aluminum, at an infinite dilution, is considered. The activity coefficients are evaluated on the basis of the sub-regular solution model assumption by using the data for O, Si, Mn, Al in pure Fe and Ni melts only. From the obtained results it seems that the activity coefficients of both silicon and aluminium are decreasing, while the activity coefficient of oxygen is increasing, with the increase of the nickel content, and that the strongest effect occurs for aluminium.

Keywords: iron-nickel melts, subregular solution model, activity coefficients, interaction parameters

Rozważono wpływ zawartości niklu w ciekłym stopie Fe-Ni na współczynniki aktywności tlenu oraz takich odtleniaczy jak mangan, krzem i glin, w roztworze o nieskończenie dużym rozcieńczeniu. Współczynniki aktywności zostały obliczone przy założeniu modelu roztworu subregularnego, jedynie w oparciu o dane dla O, Si, Mn, Al w czystych Fe i Ni. Z otrzymanych wyników wynika, iż zarówno aktywność krzemu jak i glinu maleje, w przeciwieństwie do rosnącej aktywności tlenu, w przypadku rosnącej zawartości niklu w stopie Fe-Ni, a efekt ten jest najsilniejszy dla glinu.

1. Introduction

Nickel-iron alloys, owing to their unique properties, are widely used in many industrial sectors. For example, such products as shadow kinescope masks CRT (cathode-ray tube), semiconductor integrated circuits, cores of transmission transformers, bimetallic thermometers or membrane type storage tanks for LNG (liquefied natural gas) are produced on the basis of nickel-iron alloys. The Fe-Ni alloy composed of 34÷36% nickel and up to 0.3% carbon shows a very low thermal expansion in the temperature range of (-50°C, +100°C). Owing to this feature, that alloy, called "invar" (from: Invariable Alloy), is of great significance.

Fe-Ni alloys used for special purpose materials require very deep deoxidation with the precise control of some types of oxide inclusions formed during cooling and solidification processes. To predict the concentration of oxygen and deoxidisers such as manganese, silicon and aluminum, in Fe-Ni melts in equilibrium with deoxidation products, the knowledge of the effect of the nickel content on the activity coefficients of solutes is necessary.

Although many experimental studies have been done on Fe-Ni melts for years, the activity coefficient data are not yet available in the whole range of nickel content because of the high costs and great difficulties of high-temperature experiments. Therefore, it is essential to be able to estimate the activity coefficients and interaction parameters in Fe-Ni melts with the help of theoretical models, on the basis of the knowledge of the data in pure Fe and Ni melts only.

The aim of this article is to analyse the activity coefficients of Mn, Si and Al at an infinite dilution in Fe-Ni melts at 1873K within the whole nickel concentration range, with the special attention given to Fe-36%Ni (invar).

The activity coefficient of solute "*i*" at an infinite dilution, γ_i^o, is the limit of γ_i at $X_i \to 0$

$$\gamma_i^o = \lim(\gamma_i)_{\chi_i \to 0}, \tag{1}$$

where γ_i is Raoultian activity coefficient defined as

$$\gamma_i = \frac{a_i}{X_i} \tag{2}$$

with X_i – the mole fraction of "*i*", a_i – the chemical activity, and where pure substance is chosen as a standard state.

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2. Brief review of activity coefficient models in alloys

There are many thermodynamic models which are applied in practice to solutions in which one metal is a solvent and the concentrations of solutes, metallic or nonmetallic, are restricted to small values. The formulae for the activity coefficients of solutes "i" at an infinite dilution, γ_i^o, coming from the most common models used in metallic systems are summarized below. For simplicity, the interaction parameters of a higher order than the first ones will be neglected in all the below given equations. Symbol Me denotes a solvent.

– Wagner's model ([1] cited in [2]):

$$\ln\gamma^o_{i(\mathrm{Me})} = \ln\gamma_{i(\mathrm{Me})} - \varepsilon_i^j X_j, \tag{3}$$

where ε_i^j is the first-order interaction parameter "j" upon "i", based on the mole fraction.

– Unified Interaction Parameter Model (UIPM) [3]:

$$\ln\gamma^o_{i(\mathrm{Me})} = \ln\gamma_{i(\mathrm{Me})} - \ln\gamma_{\mathrm{Me}} - \varepsilon_{i,j}X_j \tag{4}$$

$$\ln\gamma_{\mathrm{Me}} = -\frac{1}{2}\varepsilon_{i,j}X_iX_j, \tag{5}$$

where $\varepsilon_{i,j}$ is Pelton and Bale interaction parameter between "i" and "j", based on the mole fraction. UIPM model is more suitable for concentrated solutions than Wagner's equation.

– Regular Solution Model

The basis of the model, first set by Hildebrand, is an assumption that the excess entropy of mixing is zero and the excess enthalpy of mixing is non zero. Therefore the excess Gibbs free energy of mixing equals [4]:

$$\Delta G_i^{ex} = \Delta H_i^{ex} = RT\ln\gamma_{i(\mathrm{Me})} \tag{6}$$

and the activity coefficient of "i" becomes

$$\ln\gamma_{i(\mathrm{Me})} = \frac{\alpha_{i-j}X_j^2}{RT}, \tag{7}$$

where α_{i-j} is the interaction parameter between "i" and "j". As a strictly regular solution does not exist, the regular solution is modified by adding a correction term (the so called conversion factor), even if the interaction parameters between the three solutes are included in the equation.

– Darken's Quadratic Formalism [5] has the form:

$$\ln\gamma^o_{i(\mathrm{Me})} = \ln\gamma_{i(\mathrm{me})} + 2\alpha_{\mathrm{Me}-i}X_i - (\alpha_{i-j} - \alpha_{\mathrm{Me}-i} - \alpha_{\mathrm{Me}-j})X_j - \alpha_{\mathrm{Me}-i}X_i^2 - \alpha_{\mathrm{Me}-j}X_j^2 - (\alpha_{\mathrm{Me}-i} + \alpha_{\mathrm{Me}-j} - \alpha_{i-j})X_iX_j, \tag{8}$$

where α_{i-j} are Darken interaction parameters.

The mutual relations exist between Wagner and Darken interaction parameters. For example, the first-order parameters obey the following equation [5]:

$$\varepsilon^j_{i(\mathrm{Me})} = \alpha_{i-j} - \alpha_{\mathrm{Me}-i} - \alpha_{\mathrm{Me}-j} \tag{9}$$

– Darken's Quadratic Formalism with Redlich-Kister type polynomial [6,7]:

Excess Gibbs free energy of mixing is expressed by Redlich-Kister polynomial

$$\Delta G_i^{ex} = X_1X_2[{}^0\Omega_{1-2} + {}^1\Omega_{1-2}(X_1 - X_2)] \tag{10}$$

and

$$\ln\gamma^o_{i(\mathrm{Me})} = \frac{{}^0\Omega_{\mathrm{Me}-i} + {}^1\Omega_{\mathrm{Me}-i}}{RT}, \tag{11}$$

where ${}^0\Omega_{i-j}$, ${}^1\Omega_{i-j}$ are binary interaction parameters of Redlich-Kister polynomial.

– Sub-Regular Solution

This model will be applied in the present study for the estimation of the activity coefficients of solutes in a binary alloy. Considering Fe-Ni melt, the equation for the activity coefficient of solute "i" at an infinite dilution, $\gamma^o_{i(Fe-Ni)}$, takes the form [8]:

$$\ln\gamma^o_{i(\mathrm{Fe\text{–}Ni})} = X_{\mathrm{Fe}}\ln\gamma^o_{i(\mathrm{Fe})} + X_{\mathrm{Ni}}\ln\gamma^o_{i(\mathrm{Ni})} + X_{\mathrm{Fe}}X_{\mathrm{Ni}}[X_{\mathrm{Ni}}(\ln\gamma^o_{i(\mathrm{Ni})} - \ln\gamma^o_{i(\mathrm{Fe})} + \varepsilon^{\mathrm{Fe}}_{i(\mathrm{Ni})}) + X_{\mathrm{Fe}}(\ln\gamma^o_{i(\mathrm{Fe})} - \ln\gamma^o_{i(\mathrm{Ni})} + \varepsilon^{\mathrm{Ni}}_{i(\mathrm{Fe})})], \tag{12}$$

where $\gamma^o_{i(Fe)}$ – the activity coefficient of "i" at an infinite dilution in iron being the solvent, $\gamma^o_{i(Ni)}$ – the activity coefficient of "i" at an infinite dilution in nickel as the solvent, $\varepsilon^{\mathrm{Ni}}_{i(\mathrm{Fe})}$ – the first-order interaction parameter between Ni and "i" in iron, $\varepsilon^{\mathrm{Fe}}_{i(\mathrm{Ni})}$ – the first-order interaction parameter between Fe and "i" in nickel.

Other models such as "central atoms" or quasichemical ones arise from very strict theoretical descriptions of the solution structure and their final equations cannot be given in simplified forms.

3. Calculation procedure for γ_i^o in Fe-Ni melts

Assuming that the sub-regular model is suitable for Fe-Ni melts, the activity coefficients of O, Mn, Si and Al at an infinite dilution will be calculated using formula (12) in the whole range of Ni-content, and the results will be compared with the experimental data and the results obtained in [8,10]. In order to obtain the proper results from the equation (12), one needs the reliable values of $\gamma^o_{i(\mathrm{Fe})}$, $\gamma^o_{i(\mathrm{Ni})}$, $\varepsilon^{\mathrm{Ni}}_{i(\mathrm{Fe})}$ and $\varepsilon^{\mathrm{Fe}}_{i(\mathrm{Ni})}$. However, these values, determined by different research centres and cited in the literature, show a wide scattering. It especially refers to

nickel melts because the experimental studies in nickel solutions are much less carried out than in iron ones. Due to these facts, it was necessary to analyse the available literature data in detail, as to choose the most proper input data. The whole analysis is presented in [9] and Table 1 lists ln γ_i^o values, in ascending order, for oxygen, manganese, silicon and aluminium in molten Fe and Ni at 1873K. All the values referring to molten nickel that are available in the scientific literature are reviewed in Table 1. As one can see, the values in molten nickel are varying in a large range. The bold-faced data in Table 1 are those which were chosen for the sub-regular model calculations in this work. It is worth noticing that, in the case of molten iron, the bold-faced data are recommended by the research centre [11] on the basis of the optimization procedure.

The values of ln γ_i^o applied in the present paper for calculating $\gamma_{i(Fe-Ni)}^o$ from equation (12) and those used in [8,10] are compared in Table 2.

TABLE 1

Review of activity coefficients of elements at infinite dilution in molten Fe and Ni at 1873K

i	ln γ_i^o (Fe)	Investigated or recommended by		ln γ_i^o (Ni)
O	-6.06	Schenck and Gerdom	Schenck, Steinmetz, Rhee	-2.76
	-4.684	Belov et al.		
	-4.658	Jung et al.	Belton, Tankins	-2.319
	-4.648	Tanahashi et al.	Belov, Novokhatskij, Lobanov	-1.327
	-4.605	Tankins and Gokcen		
	-4.598	Schenck, Steinmetz, Rhee		-1.285
	-4.59	Ishii and Ban-ya	Miki, Hino	**-1.09**
			Bowers	-1.039
	4.556	Aleksandrov et al., Dashevskii et al.		-1.03
	-4.52	Janke and Fischer	Tankins, Gokcen	-0.989
	-4.504	Floridis and Chipman		
	-4.49	Shibaev et al.		
	-4,437	Fischer, Janke, Ackermann		-0.97
	-4.311	Fischer and Janke	Ishii, Ban-ya	-0.955
			Wriedt, Chipman	-0.663
Mn	-0.405	Arita and Pierre	Jacob	-3.17
	0	Jung, et al.		
	0.262	Sigworth, Elliott	Sigworth, Elliott	**0**
	0.285	Kubaschewski, Alcock		
	0.322	Hultgren et al.	Dashevskii et al.	0.405
	0.365	Mukai, Aide, Kitajima		
	0.405	Mathew et al.		
Si	-6.660	Miki, Hino		**-9.411**
	-6.645	Sigworth, Elliott	Ishii, Ban-ya	-9.316
	-6.28	Jung et al.	Schwerdtfeger, Engell	-9.21
	-6.27	Shibaev et al.	Tarakanov et al.	-8.874
	-5.991	Schwerdtfeger, Engell	Fujiwara, Sugiura	-4.605
Al	-3.54	Sigworth, Elliott	Dyubanov et al.	-8.74
	-3.016	Ichise, Yamauchi, Mori	Sigworth, Elliott	-8.517
	-2.856	Jung et al.	Ban-ya	**-8.422**
	-2.847	Kubaschewski, Alcock	Vachet et al.	-6.948

TABLE 2
Comparison between $\ln\gamma_i^o$ values for oxygen, manganese, silicon and aluminum in molten Fe and Ni at 1873K used in the present study and in [8,10]

	Used in this study		Used by Dashevskii V. Ya. et al. [8, 10]	
	Iron	Nickel	Iron	Nickel
$\ln\gamma_O^o$	– 4.658[11]	– 1.09[12]	– 4.56[8]	– 1.03[8]
$\ln\gamma_{Mn}^o$	0[11]	0[13]	0.365[8]	0.405[8]
$\ln\gamma_{Si}^o$	-6.28[11]	-9.411[7]	-6.645[8]	-9.316[8]
$\ln\gamma_{Al}^o$	-2.856[11]	-8.412[14]	-3.016[10]	-8.422[10]

The interaction parameters based on mole fractions, $\varepsilon_{i(Fe)}^{Ni}$ and, $\varepsilon_{i(Ni)}^{Fe}$ for dissolved species "*i*" were calculated from Wagner's interaction coefficients $e_{i(Fe)}^{Ni}$ and $e_{i(Ni)}^{Fe}$ according to the following equations

$$\varepsilon_{i(Fe)}^{Ni} = (230M_{Ni}/M_{Fe}) \cdot e_{i(Fe)}^{Ni} + (M_{Fe} - M_{Ni})/M_{Fe} \quad (13)$$

$$\varepsilon_{i(Ni)}^{Fe} = (230M_{Fe}/M_{Ni}) \cdot e_{i(Ni)}^{Fe} + (M_{Ni} - M_{Fe})/M_{Ni} \quad (14)$$

and the cross-relations are as follows:

$$\varepsilon_{i(Fe)}^{Ni} = \varepsilon_{Ni(Fe)}^{i} \quad (15)$$

$$\varepsilon_{i(Ni)}^{Fe} = \varepsilon_{Fe(Ni)}^{i} \quad (16)$$

The $\varepsilon_{i(Me)}^{j}$ values applied in this work are listed in Table 3 along with the ones used in [8,10]. Because no experimental data are available for Mn-Fe and Si-Fe interactions in liquid nickel, the values of $e_{Mn(Ni)}^{Fe}$ and $e_{Si(Ni)}^{Fe}$ are supposed to be zero for both sets of parameters presented in Table 3. The detailed review of the interaction parameters data in iron and nickel and the analysis of the choice made for the purpose of this work are included in [9].

TABLE 3
Comparison between $e_{i(Fe)}^{Ni}$ and $e_{i(Ni)}^{Fe}$ values for oxygen, manganese, silicon and aluminum in molten Fe and Ni at 1873K used in the present study and in [8,10]

	Used in this study	Used by Dashevskii V. Ya. et al. [8, 10]
$e_{O(Fe)}^{Ni}$	0.003[15]	0.006
$e_{O(Ni)}^{Fe}$	-0.025[16]	0.025
$e_{Mn(Fe)}^{Ni}$	-0.0085[17]	-0.0072
$e_{Mn(Ni)}^{Fe}$	0[8]	0
$e_{Si(Fe)}^{Ni}$	0.001[18]	0.001
$e_{Si(Ni)}^{Fe}$	0[19]	0
$e_{Al(Fe)}^{Ni}$	-0.029[17]	-0.0376
$e_{Al(Ni)}^{Fe}$	0.00045[15]	0.00045

On the basis of the equation (12) and the data presented in Tables 1-3, the calculations of activity coefficients of O, Mn, Si and Al at an infinite dilution in the Ni-Fe melts at 1873K, within the whole range of Ni-contents, were carried out. The obtained results are plotted in Figs 1-4 and compared with those proposed in [8,10] and, in the case of oxygen, also with the experimental and other theoretical results. In all the figures, some of the data points coming from Table 1 are also marked on the axis.

The calculated curve for oxygen, presented in Fig.1, is compared with the two experimental [16,21] and two theoretical [8,20] results. The experimental data differ much from each other. Fischer's data [16] are very close to the curve, except for the range of Ni up to 20% Ni. As regards the theoretical calculations, both authors have obtained slightly different results, in spite of the fact that they have applied the same sub-regular model equation. This arises from the fact that the interaction parameters and activity coefficients, $\ln\gamma_{O(Fe)}^o$, $\ln\gamma_{O(Ni)}^o$, values used by the authors were different. Aleksandrov's results [20] are in a better agreement with the present curve than the results of [8].

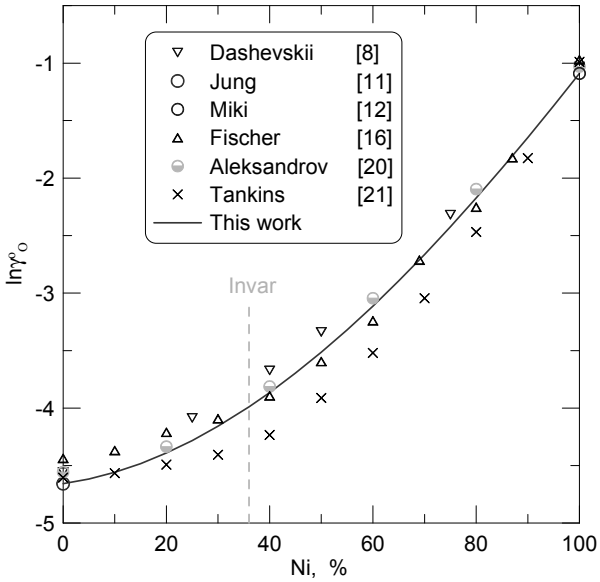

Fig. 1. Activity coefficient of oxygen at an infinite dilution in liquid Fe-Ni alloy at 1873K

The curve of $\ln\gamma_{Mn}^o$ against Fe-Ni alloy composition is plotted in Fig.2 in comparison with the calculated results obtained by [8] from the same model (eq. 12). It is worth noticing that the curve in Fig.2 has a non-monotonic form with a minimum, as opposed to the curves for oxygen, silicon and aluminum, which are monotonic (Figs.1, 3 and 4). The results proposed by [8] completely differ from the present curve because they are based on the different input parameters. For example, in

iron we have used ln $\gamma^o_{\mathrm{Mn(Fe)}}$ = 0 instead of 0.285 taken in [8], because several authors [11] consider the Fe-Mn melt as almost an ideal solution. Nevertheless, in spite of the different data used, the final results obtained by [8] show a minimum too.

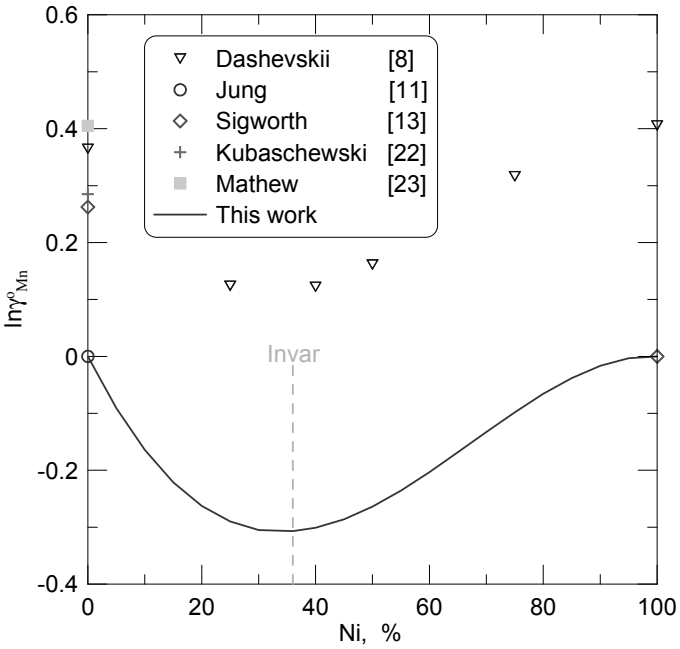

Fig. 2. Activity coefficient of manganese at an infinite dilution in liquid Fe-Ni alloy at 1873K

Figs. 3 and 4 show the calculated curves for silicon and aluminum, respectively, along with the results obtained by [8] and [10]. The selected measured activity coefficients data for silicon and aluminum in pure liquid nickel and iron are marked on the axes too. The published activity coefficients data for Si and Al in nickel are very limited, but one may state that both γ^o_{Si} and γ^o_{Al} values are usually lower in nickel than in iron. This effect appears to be much stronger for aluminum than for silicon. In the case of the data used in this work, the (ln $\gamma^o_{i(\mathrm{Fe})}$ – ln $\gamma^o_{i(\mathrm{Ni})}$) value equals about 2.8 for Si and 5.5 for Al. The curves in Figs 3 and 4 are monotonic and, with the increase of nickel content in Fe-Ni, the activity coefficients of Si and Al are decreasing. The decrease of ln $\gamma^o_{i(\mathrm{Fe–Ni})}$ for silicon with the nickel content increase is slower in the Fe-rich region, so the Si-curve shows up convexity, as opposed to the Al-curve which is down convex (like the oxygen-curve in Fig.1).

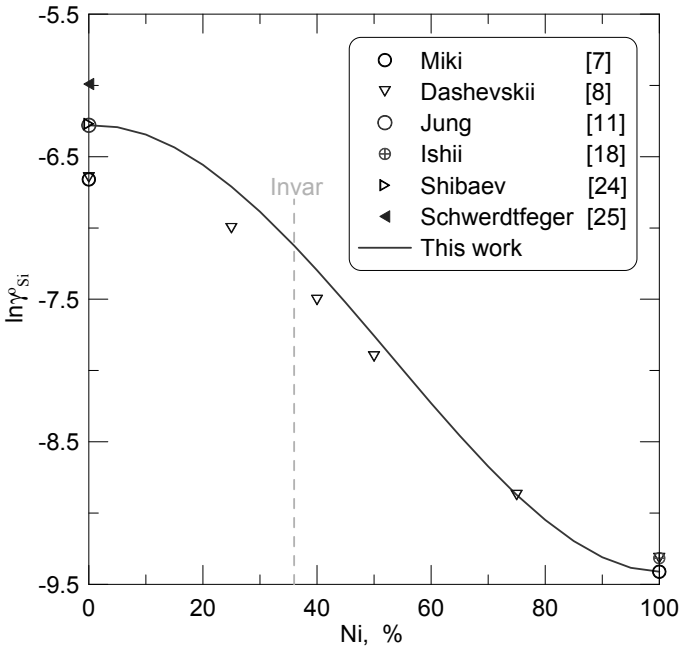

Fig. 3. Activity coefficient of silicon at an infinite dilution in liquid Fe-Ni alloy at 1873K

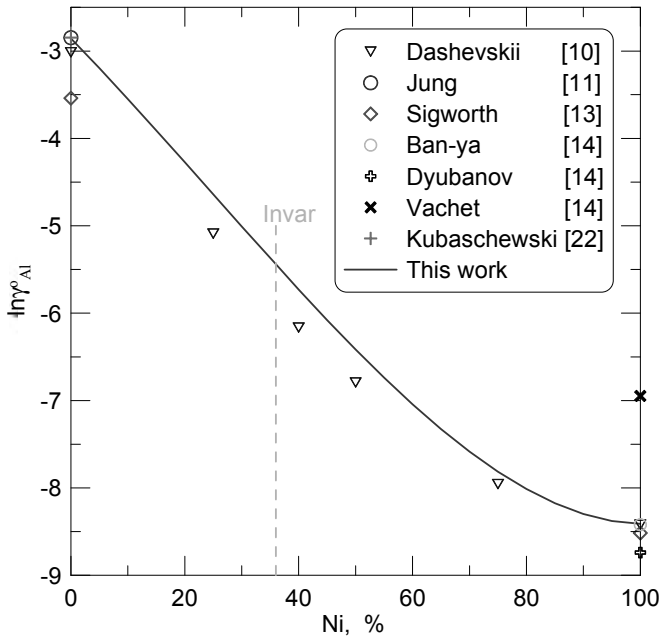

Fig. 4. Activity coefficient of aluminum at an infinite dilution in liquid Fe-Ni alloy at 1873K

4. Activity coefficients and interaction parameters in liquid Fe-36%Ni

The calculation procedure was applied to Fe-36%Ni, an alloy of great technical use, and the calculated values of ln $\gamma^{\mathrm{o}}_{\mathrm{i}}$ are listed in Tab.4.

TABLE 4
Activity coefficients of O, Mn, Si, Al at an infinite dilution in Fe-36%Ni at 1873K

	Fe-36%Ni
$\ln \gamma_O^o$	-3.989
$\ln \gamma_{Mn}^o$	-0.308
$\ln \gamma_{Si}^o$	-7.124
$\ln \gamma_{Al}^o$	-5.444

By taking liquid Fe-36%Ni as a solvent, the first-order interaction parameters, $\varepsilon_{i(\mathrm{Fe-Ni})}^{j}$, between oxygen, manganese, silicon and aluminum, were calculated from the assumption [8]

$$\varepsilon_{i(\mathrm{Fe-Ni})}^{j} = X_{Fe}\varepsilon_{i(\mathrm{Fe})}^{j} + X_{\mathrm{Ni}}\varepsilon_{i(\mathrm{Ni})}^{j} \tag{17}$$

and afterwards converted to parameters $e_{i(\mathrm{Fe-Ni})}^{j}$ according to

$$\varepsilon_{i(\mathrm{Fe\text{-}Ni})}^{j} = (230M_j/M_{Fe\text{-}Ni}) \cdot e_{i(\mathrm{Fe\text{-}Ni})}^{j} + (M_{Fe\text{-}Ni} - M_j)/M_{Fe\text{-}Ni}, \tag{18}$$

where

$$M_{\mathrm{Fe-Ni}} = X_{Fe}M_{\mathrm{Fe}} + X_{\mathrm{Ni}}M_{\mathrm{Ni}}. \tag{19}$$

The results are listed in Tab.5 where the blanks denote that the appropriate $\varepsilon_{i(\mathrm{Ni})}^{j}$ or $e_{i(\mathrm{Ni})}^{j}$ values in nickel were not known. The values of $e_{i(\mathrm{Ni})}^{j}$ used were: $e_{\mathrm{O(Ni)}}^{\mathrm{Mn}}$ = -0.450, $e_{\mathrm{O(Ni)}}^{\mathrm{Si}}$ = -0.065, $e_{\mathrm{O(Ni)}}^{\mathrm{Al}}$ = -1.470, $e_{\mathrm{O(Ni)}}^{\mathrm{O}}$ = 0, $e_{\mathrm{Mn(Ni)}}^{\mathrm{Mn}}$ = 0.006, $e_{\mathrm{Si(Ni)}}^{\mathrm{Si}}$ = 0.190, $e_{\mathrm{Al(Ni)}}^{\mathrm{Al}}$ = 0.085.

TABLE 5
First-order interaction parameters e_i^j between O, Mn, Si, and Al in Fe-36%Ni at 1873 K

		Fe–36 %Ni			
		i			
	j	**O**	**Mn**	**Si**	**Al**
e_i^j	O	-0.116	-0.571	-0.116	-2.150
	Mn	-0.166	0.002	–	0.034
	Si	-0.066	–	0.132	–
	Al	-1.272	0.064	–	0.04

5. Conclusion

Although the number of measurements carried out in nickel solutions is very limited and the experimental data differ between themselves significantly, the calculations presented in this paper enable to estimate the activity coefficients of solutes in Fe-Ni alloy, especially in Fe-36%Ni one.

The logarithm of the activity coefficient for oxygen, silicon and aluminum at an infinite dilution in Fe-Ni melts, achieved in this paper on the basis of the sub-regular model, behaves as follows:

– is increasing for oxygen,
– is decreasing for both silicon and aluminum, but in a higher degree for aluminum,
– is passing through a minimum for manganese (which is rather unexpected and probably derives from the fact that the activity coefficient curve at 0% Ni and 100% Ni has the same value i.e. $\gamma_{\mathrm{Mn(Fe)}}^{o} = \gamma_{\mathrm{Mn(Ni)}}^{o}$), with the increase of nickel content in Fe-Ni melt.

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List of symbols

a_i – activity of species "i" with reference to a specified standard state,
e_i^j – the first-order interaction parameter of "j" upon "i", on the basis of the mass percentage,
M_{Ni}, M_{Fe} – molecular mass of nickel, iron,
R – ideal gas constant,
T – temperature, K
X_i – mole fraction of species "i",
α_{i-j} – Darken interaction parameter between "i" and "j",
γ_i – Raoultian activity coefficient of solute "i"in a metallic solution, on the basis of the mole fraction,
γ_i^o – Raoultian activity coefficient of solute "i"at an infinite dilution, on the basis of the mole fraction,
ε_i^j – the first-order interaction parameter "j" upon "i", on the basis of the mole fraction,
$\varepsilon_{i,j}$ – Pelton and Bale interaction parameter between "i" and "j", on the basis of the mole fraction,
ΔG^{ex} – excess Gibbs energy of mixing,
ΔH^{ex} – excess enthalpy of mixing,
${}^0\Omega_{i-j}$, ${}^1\Omega_{i-j}$ – binary interaction parameters of Redlich-Kister polynomial.

REFERENCES

[1] C. Wagner, Thermodynamic of Alloys, Addison – Wesley Press, Cambridge, MA, 51-53 (1952).
[2] Z. Ma, Metallurgical and Materials Transaction B **32B**, 87-103 (1997).
[3] C. W. Bale, A. D. Pelton, Metallurgical and Materials Transaction A **21A**, 1997-2002 (1990).
[4] J. H. Hildebrand, Proceedings of the National Academy of Sciences **13**, 267-272 (1927).
[5] L. S. Darken, Trans. Met. Soc. AIME **239**, 90-96 (1967).
[6] N. Saunders, A. P. Miodownik, Calphad (Calculation of Phase Diagrams) A Comprehensive Guide, Pergamon, Oxford, 91-128 (1988).
[7] T. Miki, M. Hino, ISIJ Int. **44**, 1800-1809 (2004).
[8] V. Ya. Dashevskii, A. M. Katsnelson, N. N. Makarova, V. I. Kashin, ISIJ Int. **43**, 1487-1494 (2003).
[9] W. Jerzak, Doctor's thesis, Kraków, (2008).
[10] V. Ya. Dashevskii, N. N. Makarova, K. V. Grigorovitch, A. G. Kanevskii, V. I. Kashin, ISIJ Int. **45**, 8-11 (2005).
[11] I.-H. Jung, S. A. Decterov, A. D. Pelton, Metallurgical and Materials Transaction B **35B**, 493-507 (2004).
[12] T. Miki, M. Hino, ISIJ Int. **45**, 1848-1855 (2005).
[13] P. C. Hayes, Process Principles in Minerals and Materials Production, Third Edition, School of Engineering of Queensland, Brisbane, Australia, (2003).
[14] F. Ishii, S. Ban-ya, M. Hino, ISIJ Int. **36**, 25-31 (1996).
[15] S.-W. Cho, H. Suito, Steel Research **66**, 237-243 (1995).
[16] W. A. Fischer, D. Janke, W. Ackermann, Archiv für das Eisenhüttenwesen **41**, 361-367 (1970).
[17] H. Ohta, S. Suito, ISIJ Int. **43**, 1301-1308 (2003).
[18] F. Ishii, S. Ban-ya, ISIJ Int. **32**, 1091-1096 (1992).
[19] S. Ban-ya, F. Ishii, D. Ohtaki, ISIJ Int. **34**, 484-490 (1994).
[20] A. A. Aleksandrov, M. A. Makarov, V. Ya. Dashevskii, Izvestiâ Akademii Nauk SSSR Metally **4**, 3-10 (2006).
[21] E. S. Tankins, N. A. Gokcen, Metallurgical Transactions **2**, 1605-1611 (1971).
[22] O. Kubaschweski, C. B. Alcock, Metallurgical Thermochemistry, 5th Edition, Pergamon Press (1979).
[23] P. M. Mathew, M. L. Kapoor, M. G. Frohberg, Archiv für das Eisenhüttenwesen **43**, 865-872 (1972).
[24] S. S. Shibaev, P. V. Krasovskii, K. V. Grigorovitch, ISIJ Int. **45**, 1243-1247 (2005).
[25] T. Fujisawa, K. Imaoka, H. Sakao, Transaction of the Iron and Steel Institute of Japan **21**, 559-567 (1981).

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