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DETERMINATION OF THE STABILITY OF $Al_{11.8}FeMn_{1.6}Si_{1.6}$ PHASE EXISTING IN THE QUATERNARY Al–Fe–Mn–Si SYSTEM

OKREŚLENIE STABILNOŚCI FAZY $Al_{11.8}FeMn_{1.6}Si_{1.6}$ WYSTĘPUJĄCEJ W UKŁADZIE CZTEROSKŁADNIKOWYM Al–Fe–Mn–Si

Using regular solution model the thermodynamic stability of the phase $Al_{11.8}FeMn_{1.6}Si_{1.6}$ was assessed in the temperature range 878—973 K. In order to calculate activities of components in the liquid phase remaining in equilibrium with the solid phase, experimentally determined liquidus composition were used together with literature data available for respective binary systems. It was assumed that in the limited range of concentrations thermodynamic properties of binary liquid solutions obey regular solution behaviour. Temperature dependence of the G i b b s free energy change derived for the reaction of formation of the $Al_{11.8}FeMn_{1.6}Si_{1.6}$ phase using regular solution model takes the form:

$$\Delta G^0 = -416.7 + 0.0654 \cdot T \text{ kJ/mol}.$$

Posługując się modelem roztworów regularnych do opisu właściwości termodynamicznych fazy ciekłej, określono stabilność termodynamiczną fazy stałej o składzie $Al_{11.8}FeMn_{1.6}Si_{1.6}$ w zakresie temperatur 878—973 K. Celem obliczenia aktywności składników w roztworze ciekłym pozostającym w równowadze z fazą stałą użyto składów wyznaczonej doświadczalnie linii likwidus wraz z danymi literaturowymi odnośnie do termodynamiki poszczególnych układów podwójnych. Założono, że w roztworze ciekłym w ograniczonym zakresie stężeń własności termodynamiczne składników zachowują się zgodnie z modelem roztworów regularnych. Zależność temperaturowa zmiany energii swobodnej G i b b s a wyznaczonej dla reakcji tworzenia fazy stałej $Al_{11.8}FeMn_{1.6}Si_{1.6}$ jest opisana równaniem:

$$\Delta G^0 = -416.7 + 0.0654 \cdot T \text{ kJ/mol}.$$

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1. Introduction

The knowledge of phase equilibria in the quaternary Al–Fe–Mn–Si as well as conditions of intermetallic phases formation are necessary for advances in technology of the refinement of Al–Si alloys from iron using electrothermic process. Though it is well known that iron rich intermetallic phases are deleterious inclusions in most of the commercial aluminium alloys [1—4], controlled precipitation of some iron-rich intermetallic phases can be used to obtain commercial purity Al–Si alloys starting up from scraps.

Despite of the availability of technical information for most of the Al–Fe–Mn–Si alloys, there is still a lack of thermodynamic data for many of the well-known phases existing in this system. This may be a main obstacle to understand processes of impurity removal.

Information about the relevant phase equilibria in the quaternary system is scarce. Zakharov et al. [5, 6] investigated phase relations in Al–Si–Mn and Al–Si–Fe systems as well as in the quaternary Al–Fe–Mn–Si system [7, 8]. The range of investigated compositions varied from 10 to 14 wt. pct Si, 0.3 wt. pct Fe and from 0 to 4 wt. pct of Mn. It was shown that in the Al-rich portion of the quaternary system hexagonal quaternary phase $Al_{16}(MnFe)_4Si_3$ exists. There is also a pseudoternary $Al–Al_{16}(MnFe)_4Si_3–Si$ field, in which eutectic equilibrium

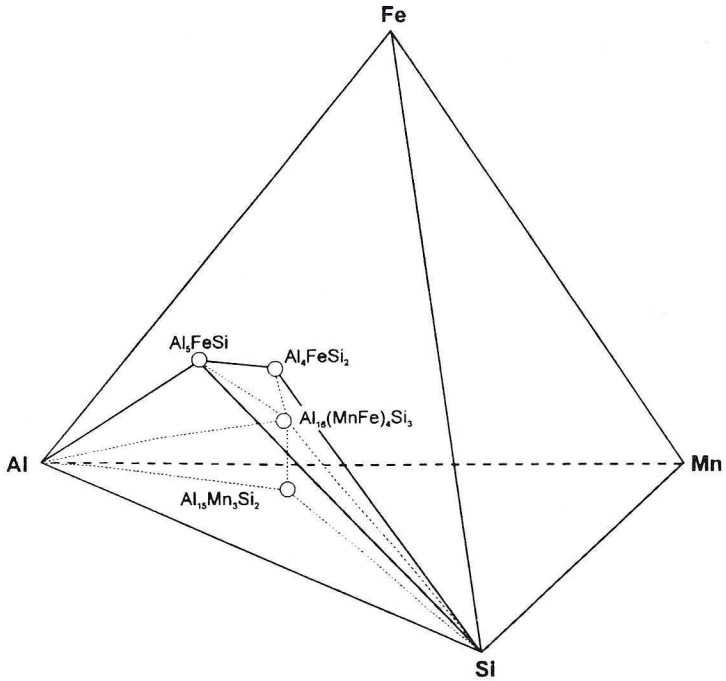


Fig. 1. Schematic representation of phase equilibria in quaternary Al–Mn–Fe–Si system

$L = \alpha - Al + Al_{16}(MnFe)_4Si_3 + Si$ takes place. The temperature of the eutectic reaction is estimated at 849 K and the corresponding eutectic composition of the liquid is: 12.4 wt.% Si, 0.36 wt.% Fe and 0.4 wt.% Mn.

Liquidus temperature in this system [7] depends on Fe and Mn concentration. For the alloy Al + 10 wt.% Si + 1 wt.% Fe this temperature is about 863 K, while with increasing Fe concentration up to 3 wt. pct. it rises up to 943 K. Addition of manganese above 4 wt. pct results in further temperature increase up to 993—1018 K. It was also found that ternary phases Al_3FeSi and $Al_{15}Mn_3Si_3$ do not form continuous solid solutions.

Schematic representation of the phase equilibria in the considered quaternary system is shown in Fig. 1, in which respective ternary phases in equilibrium with the quaternary phase are also shown. It is clear from the Zakharov's studies [8] that the addition of manganese is a factor, which decides about the formation of particular intermetallic phase in this system. Precipitates of Al8FeMnSi2 intermetallic phase observed after freezing of Al–Fe–Si alloy following Mn addition are the best example [9].

Recently, the existence of another quaternary phase $Al_{11.8}FeMn_{1.6}Si_{1.6}$ has been detected in Fe-rich corner of the quaternary system. In the present paper thermodynamic stability of this new phase is estimated.

2. Experimental

The methodology of experiments carried out on the precipitation and identification of a new $Al_{0.662}Si_{0.173}Mn_{0.082}Fe_{0.081}$ (formula given per g.atom) was described in the previous paper [10]. Four different alloys were chosen, whose initial compositions are shown in table 1.

TABLE 1

The initial concentrations (weight %) of Al–Fe–Mn–Si starting solutions given for four (I—IV) runs

	Al	Fe	Mn	Si
I	89.10	0.80	0.60	9.50
II	88.40	1.30	0.80	9.50
III	87.50	1.50	1.50	9.50
IV	86.70	1.60	2.20	9.50

These alloys were melted and then kept at constant temperature of 878, 909, 918, 946 and 973 K. It was found experimentally that at 1073 K all samples were liquid. After the time necessary for phase precipitation and attainment of the equilibrium state (bout 6 h) the sample was withdrawn and cooled down quickly in air. The

composition of the frozen alloy as well as the remaining liquid corresponded to solid-liquid equilibrium below liquidus in the quaternary system. The samples were cut into 4 layers (I—IV) and analysed using X-ray diffraction and chemical analysis. This procedure let the composition of the solid phase as well as the solidified liquid be determined for each sample layer. The results obtained in this way yield the composition of the liquid phase after its separation from the solid phase below liquidus temperature. They are gathered in table 2.

TABLE 2

The points of the liquidus hyper-surface for four (I—IV) runs (weight %) and for five different temperatures

878 K	Al	Fe	Mn	Si
I	89.46	0.66	0.55	9.33
II	89.48	0.68	0.54	9.30
III	90.00	0.59	0.60	8.81
IV	90.68	0.36	0.49	8.47

909 K	Al	Fe	Mn	Si
I	89.42	0.67	0.55	9.36
II	89.36	0.76	0.56	9.32
III	89.87	0.63	0.65	8.82
IV	89.83	0.59	0.86	8.72

918 K	Al	Fe	Mn	Si
I	89.27	0.69	0.57	9.47
II	89.16	0.83	0.64	9.37
III	89.67	0.69	0.68	8.96
IV	89.21	0.70	1.08	9.01

946 K	Al	Fe	Mn	Si
I	89.19	0.74	0.58	9.49
II	88.99	0.91	0.71	9.39
III	88.85	0.91	0.93	9.31
IV	88.71	0.89	1.56	8.84

973 K	Al	Fe	Mn	Si
I	--	--	--	no compound
II	88.85	0.99	0.73	9.43
III	88.40	1.11	1.16	9.33
IV	88.11	1.10	1.79	9.00

The EDX microprobe analysis of the precipitated solid phase taken as an average of more than 50 analysed compositions let the stoichiometry of the solid phase be established as $Al_{11.8}Si_{1.6}Mn_{1.6}Fe$.

3. Thermodynamic properties of quaternary liquid solutions

Using experimental data given above, the G i b b s free energy of formation of the quaternary phase crystallising from the liquid solution can be derived with the aid of the liquidus temperature-phase composition dependence. However, thermodynamic properties of the liquid solutions are needed to accomplish these calculations.

Thermodynamic properties of the quaternary solutions Al-Si-Mn-Fe are not known. Since the phase appears in the Al-rich corner of the system, the range of alloy compositions under consideration covers only a small range of solute mole fraction: X_{Si}, X_{Mn} and X_{Fe}.

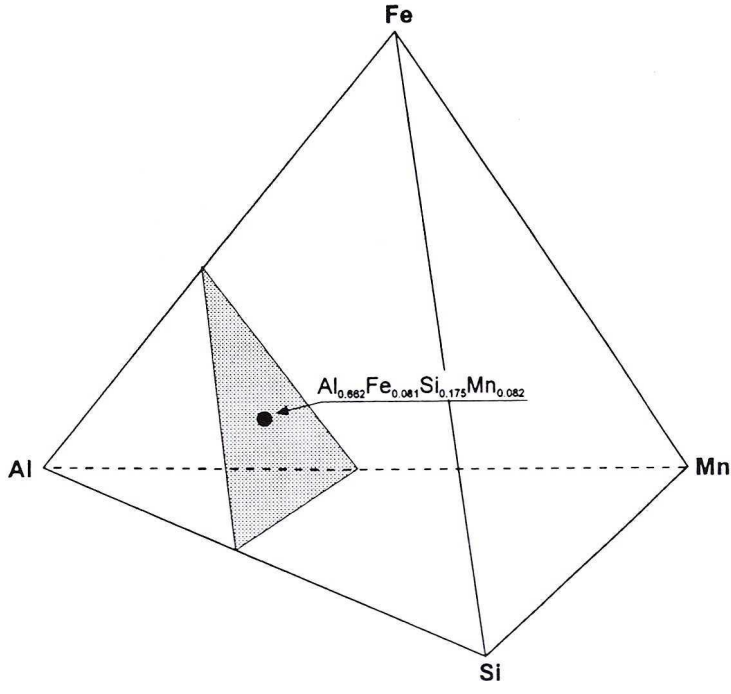


Fig. 2. Tetrahedron Al–Mn–Fe–Si with suggested location of the new phase $Al_{0.662}Si_{0.175}Mn_{0.082}Fe_{0.081}$

Fig. 2 shows schematically the location of the phase and possible range of compositions. In this situation it seems reasonable to apply to the calculations a model which:

— allows us to predict the properties of a quaternary solution from respective binaries,

— can reproduce these properties only in a small concentration range.

According to the above assumptions the regular solution model seems to be a satisfactory approximation for the description of activities in the liquid solution.

In the binary system 1—2, activity coefficients of components represented by the regular solution model [11] take the form:

$$\ln \gamma_1 = \frac{b_{12}}{R \cdot T} \cdot X_2^2 \tag{1}$$

$$\ln \gamma_2 = \frac{b_{12}}{R \cdot T} \cdot X_1^2, \tag{2}$$

where:

b_{12} is an interaction parameter characterising the 1—2 system.

Excess molar Gibbs free energy is given by the term:

$$\Delta G^E = R \cdot T \cdot (X_1 \cdot \ln \gamma_1 + X_2 \cdot \ln \gamma_2) = b_{12} \cdot X_1 X_2 . \tag{3}$$

The characteristic feature of this model is that respective binary terms can be added to yield an expression of ΔG^E for higher order systems. For example, for the ternary system we obtain:

$$\Delta G^E = b_{12} \cdot X_1 X_2 + b_{13} \cdot X_1 X_3 + b_{23} \cdot X_2 X_3 . \tag{4}$$

The main question is how to derive the expression for the activity coefficients of components in the multicomponent system. To do this one can apply the general formula:

$$\ln \gamma_j = \frac{1}{R \cdot T} \cdot \left(\frac{\partial n \Delta G^E}{\partial n_i} \right)_{P, T, n_{j \neq i}} \tag{5}$$

to the eq. 4, multiplied by the total number of moles, n:

$$n \cdot \Delta G^E = b_{12} \frac{n_1 n_2}{n} + b_{13} \frac{n_1 n_3}{n} + b_{23} \frac{n_2 n_3}{n} . \tag{6}$$

Taking derivative with respect to chosen number of moles, and after necessary rearrangements we have:

$$\ln \gamma_1 = \frac{1}{R \cdot T} \cdot \frac{\partial}{\partial n_1} \left(b_{12} \frac{n_1 n_2}{n} + b_{13} \frac{n_1 n_3}{n} + b_{23} \frac{n_2 n_3}{n} \right)_{P, T, n_2, n_3} \tag{7}$$

which yields the following expression:

$$\ln \gamma_1 = \frac{1}{R \cdot T} \cdot (b_{12} \cdot X_2^2 + b_{13} \cdot X_3^2 + (b_{12} + b_{13} - b_{23}) \cdot X_2 X_3) . \tag{8}$$

This method of calculations can be extended upon multicomponent system. Consequently, for the quaternary system we have:

$$\Delta G^E = b_{12} \cdot X_1 X_2 + b_{13} \cdot X_1 X_3 + b_{14} \cdot X_1 X_4 + \\ + b_{23} \cdot X_2 X_3 + b_{24} \cdot X_2 X_4 + b_{34} \cdot X_3 X_4, \quad (9)$$

which after necessary rearrangements yields for component "1" in the solution the following expression:

$$\ln \gamma_1 = \frac{1}{R \cdot T} \cdot (b_{12} \cdot X_2^2 + b_{13} \cdot X_3^2 + b_{14} \cdot X_4^2 + (b_{12} + b_{13} - b_{23}) \cdot X_2 X_3 + \\ + (b_{12} + b_{14} - b_{24}) \cdot X_2 X_4 + (b_{13} + b_{14} - b_{34}) \cdot X_3 X_4). \quad (10)$$

Using the above procedure one can derive a general formula for the $\ln \gamma_i$ of the i-th component in the multicomponent system:

$$\ln \gamma_i = \frac{1}{R \cdot T} \left(\sum_{j \neq i}^{n} b_{ij} \cdot X_j \cdot (1 - X_i) + \sum_{\substack{k \neq i \\ j > k}}^{n} b_{jk} \cdot X_j X_k \right) \quad \text{for } i, j, k = 1 \ldots n. \quad (11)$$

In order to assure better flexibility of the $\ln \gamma_i$ function with temperature, the term b_{ij}/RT was substituted by the equation of the type:

$$f_{ij}(T) = \left(\frac{\alpha}{T} + \beta \right). \quad (12)$$

The next step to be done is to work out the expressions for functions represented by eq. 12 for respective binary systems. Available experimental data must be used to adjust proper parameters and to make whole model reliable for activity prediction.

4. Determination of the $f_{ij}(T)$ interaction parameters for respective binary systems

The approach discussed above requires that the contributions from six binary systems should be added to describe the activity coefficients of components in liquid quaternary solution. This is illustrated in Fig. 3, which depicts respective binary systems under consideration. Consequently, experimental data from these six binary systems must be taken into account to adjust respective interaction parameters $f_{ij}(T)$ in formula (11).

a) Al–Fe system

Partial heats of solution ΔH_{Fe} and ΔH_{Al} were determined by Wooley and Elliot [12] at 1873 K, and Radcliff et al. [13] at 1173 K. Also, Eldrige and Komarek [14] gave ΔH_{Al} values at the same temperature 1173 K. Hultgren et al. [15] evaluated thermodynamic properties of the liquid Al–Fe solutions, and

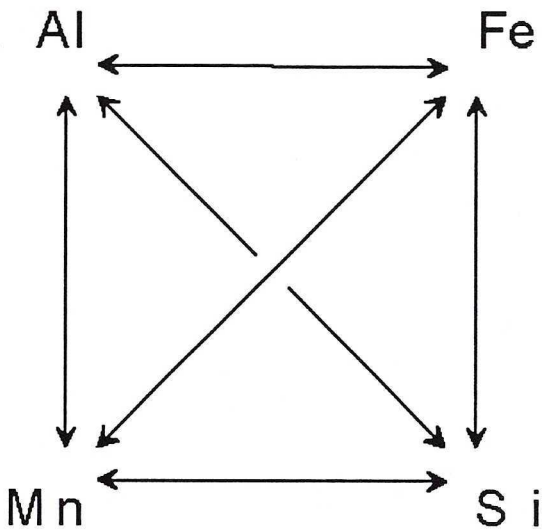


Fig. 3. Schematic representation of six binary systems which are required to describe the activity coefficients of all components in liquid quaternary solution

according to this work partial heat at infinite dilution ΔH_{Al} at $X_{Fe} = 0$ is equal to -28444 J/mole at 971 K.

Using Knudsen mass spectrometry Jacobson and Mehrotra [16] determined activity coefficients of iron at 1573 K, while Hultgren's evaluation gives activity coefficients of Al and Fe at 1873 K. Taking the data mentioned above into account, calculated temperature dependence of $f_{Al-Fe}(T)$ function is found to be:

$$f_{Al-Fe}(T) = \left(\frac{-15450}{T} + 5.3528\right). \tag{13}$$

b) Al–Mn system

Partial heat of solution ΔH_{Mn} was measured by Esin et al. [17] at 1626 K. Excess partial Gibbs free energy of Mn in the liquid solution was determined by Batalin et al. [18] who used emf method at 1570 K. These data let the parameter $f_{Al-Mn}(T)$ be evaluated for Al-rich concentration range:

$$f_{Al-Mn}(T) = \left(\frac{-8439}{T} + 2.490\right). \tag{14}$$

c) Al–Si system

The heat of mixing of the liquid Al–Si alloys was measured calorimetrically by Bues et al. [19] at 1377 K. Partial Gibbs free energy of Al was determined independently from electrochemical measurements by Schaefer and Gokcen

[20] at 1100 K, and B e r t h o n et al. [21] in wider temperature range. Using these data for Al-rich solutions one can obtain the following relationship:

$$f_{\mathrm{Al-Si}}(T) = \left(\frac{-1537}{T} - 1.6388\right). \tag{15}$$

An analysis of the quaternary system (Fig. 3) indicates that to use successfully regular solution model, interaction parameters for Fe–Mn, Fe–Si and Mn–Si binaries should be derived from experimental data obtained in the middle of concentration range of these binary systems.

d) Fe–Mn system

Binary system shows continuous solid solution extended from pure Fe to pure Mn. It seems that liquid solution should obey ideal behaviour. Experimental data of B a t a l i n et al. [22] indicate small, positive values of enthalpy of mixing. Estimated values of Mn activity in liquid Fe–Mn solutions are given by H u l t g r e n et al. [15] at 1863 K. The above information supports the view that solutions exhibit slight positive deviation from the R a o u l t ' s Law. Calculated parameter $f_{\mathrm{Fe-Mn}}(T)$ takes the simplest form:

$$f_{\mathrm{Fe-Mn}}(T) = \frac{540}{T}. \tag{16}$$

e) Fe–Si system

According to H u l t g r e n et al. [15] molar heat of mixing evaluated for 1873 K is negative. Activities of Si measured at the same temperature by F r u e h a n [23], who used emf technique with solid electrolytes, show negative deviation from R a o u l t ' s law in this solution. Using this data, interaction parameter was calculated as:

$$f_{\mathrm{Fe-Si}}(T) = \left(\frac{-16529}{T} + 7.0307\right). \tag{17}$$

f) Mn–Si system

Using vapour pressure measurements T a n a k a [24] determined the activity of manganese in solid and liquid solutions at 1673 K. In turn, E s i n et al. [25] measured molar enthalpy of mixing at 1773 K. Using these data the interaction parameter was determined as:

$$f_{\mathrm{Mn-Si}}(T) = \left(\frac{-17689.5}{T} + 4.2499\right). \tag{18}$$

The expressions obtained for interaction parameters of six binary systems were used to derive respective formulas for $\ln \gamma_i$ and molar heat of mixing , ΔH^M, which are gathered in Tab. 3. In Fig. 4 values derived with the aid of these expressions are compared with the respective experimental data obtained for these systems. A good fit is observed in this concentration range of binary alloys, which is next projected into the field of quaternary system under consideration (Fig. 2).

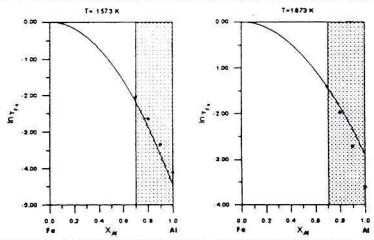
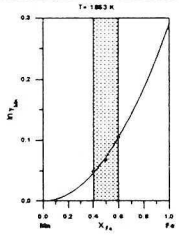
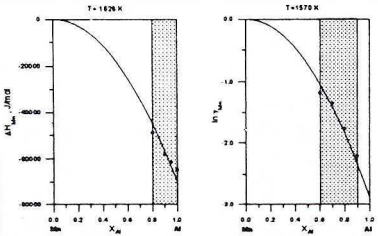
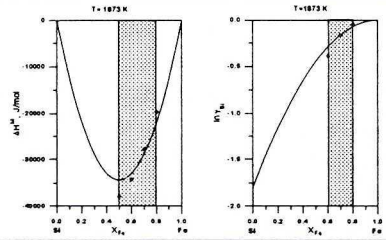
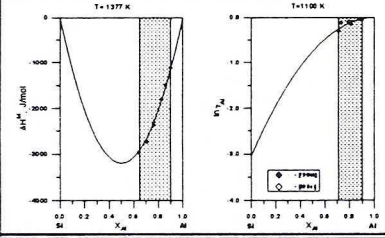
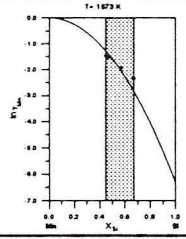
System	Figures of ΔH^M and $\ln \gamma_i$ vs. composition	System	Figures of ΔH^M and $\ln \gamma_i$ vs. composition
Al-Fe		Fe-Mn	
Al-Mn		Fe-Si	
Al-Si		Mn-Si	

Fig. 4. Integral heats of mixing (in Joules) and $\ln \gamma_i$ vs. concentration plots showing predicted and experimental values of these functions

TABLE 3

The formulas for $\ln \gamma_i$ and molar heat of mixing ΔH^M (in Joules) derived for six binary systems of Al–Fe–Mn–Si quaternary system from interaction parameters (13)–(18)

System	ΔH^M, $\ln \gamma_i$ formulas	System	ΔH^M, $\ln \gamma_i$ formulas
Al–Fe	$\Delta H^M_{Al-Fe} = -15450 \cdot R \cdot X_{Al} \cdot X_{Fe}$	Fe–Mn	$\Delta H^M_{Fe-Mn} = 540 \cdot R \cdot X_{Mn} \cdot X_{Fe}$
	$\ln \gamma_{Fe} = \left(\frac{-15450}{T} + 5.3528\right) \cdot X^2_{Al}$		$\ln \gamma_{Mn} = \frac{540}{T} \cdot X^2_{Fe}$
Al–Mn	$\Delta H^M_{Al-Mn} = -8439 \cdot R \cdot X_{Al} \cdot X_{Mn}$	Fe–Si	$\Delta H^M_{Fe-Si} = -16529 \cdot R \cdot X_{Si} \cdot X_{Fe}$
	$\ln \gamma_{Mn} = \left(\frac{-8439}{T} + 2.490\right) \cdot X^2_{Al}$		$\ln \gamma_{Si} = \left(\frac{-16529}{T} + 7.0307\right) \cdot X^2_{Fe}$
Al–Si	$\Delta H^M_{Al-Si} = -1537 \cdot R \cdot X_{Al} \cdot X_{Si}$	Mn–Si	$\Delta H^M_{Mn-Si} = -17689.5 \cdot R \cdot X_{Mn} \cdot X_{Si}$
	$\ln \gamma_{Al} = \left(\frac{-1537}{T} - 1.6388\right) \cdot X^2_{Si}$		$\ln \gamma_{Mn} = \left(\frac{-17689.5}{T} + 4.2499\right) \cdot X^2_{Si}$

5. Calculation of the Gibbs free energy change for the reaction of formation

Having liquidus compositions determined from equilibration experiments, one could calculate Gibbs free energy of formation of the solid quaternary phase. According to the chemical reaction:

$$11.8\,\underline{Al} + \underline{Fe} + 1.6\,\underline{Mn} + 1.6\,\underline{Si} = Al_{11.8}\,FeMn_{1.6}Si_{1.6}(s) \tag{19}$$

liquid phase with the liquidus composition remains in equilibrium with pure, solid phase. Using the condition of chemical equilibrium:

$$\Delta G_T = \mu^0_{Al_{11.8}FeMn_{1.6}Si_{1.6}} - (11.8\,\mu_{Al} + \mu_{Fe} + 1.6\,\mu_{Mn} + 1.6\,\mu_{Si}) = 0 \tag{20}$$

and its relation to equilibrium constant of the reaction (19):

$$\Delta G^0_T = -RT\left(\frac{1}{a^{11.8}_{Al}\, a_{Fe}\, a^{1.6}_{Mn}\, a^{1.6}_{Si}}\right) \tag{21}$$

the change in standard Gibbs free energy can be obtained.

Consequently, equation 21 can be used to accomplish this task. At constant temperature the composition of the liquidus hypersurface $\{X_{Al}, X_{Mn}, X_{Fe}, X_{Si}\}$ must correspond to the constant composition of the phase. Since these compositions are known (table 2), corresponding values of activities at this temperature can be calculated for the liquid using formulas derived in this work.

Relation (21) can be rearranged to obtain:

$$\Delta G^0_T = R \cdot T(11.8 \ln X_{Al} + \ln X_{Fe} + 1.6 \ln X_{Mn} + 1.6 \ln X_{Si}) + \\ + R \cdot T(11.8 \ln \gamma_{Al} + \ln \gamma_{Fe} + 1.6 \ln \gamma_{Mn} + 1.6 \ln \gamma_{Si}), \tag{22}$$

where respective $\ln\gamma$'s are substituted with equations (10) and using formulas (13)–(18).

Two figures 5 and 6 show the values of a change in G i b b s free energy of the reaction (19), derived in the following way:

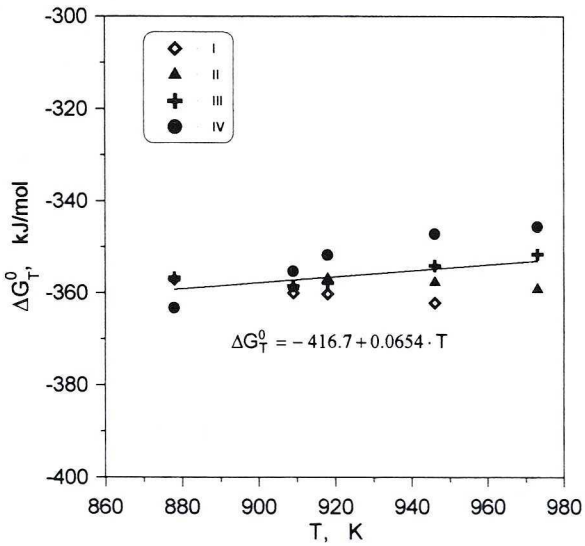


Fig. 5. G i b b s free energy change calculated for reaction (19) using regular solution model. The least-square method fit yields the temperature dependence of it

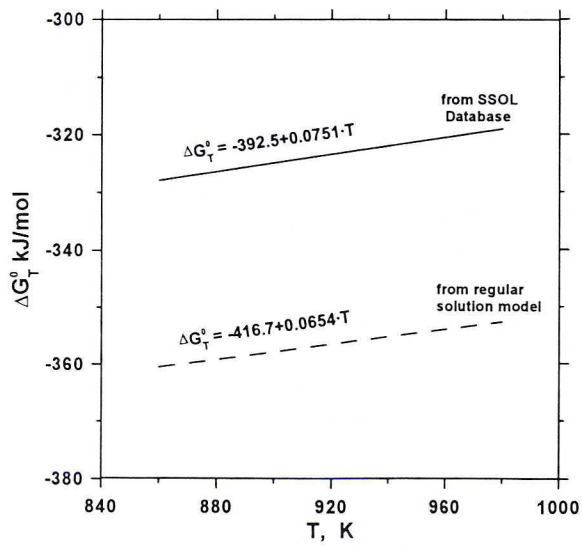


Fig. 6. Comparison between G i b b s free energy change calculated for reaction (19) with regular solution model and ThermoCalc database SSOL

— In Fig. 5 the values of ΔG^0 of the reaction (19) were calculated from eq. 22 and expressions as stated above using all available compositions given in table 2. The least-squares fit of these data yielded the following temperature dependence of the free energy change:

$$\Delta G_T^0 = -416.7 + 0.0654 \cdot T \quad \text{kJ/mole}. \tag{23}$$

— In Fig. 6. we compared calculated values of the free energy change resulting from regular solution model approach presented in this work with the values derived from Thermocalc Database SSOL. It is clear that values obtained using Thermocalc are about 30 kJ less negative than those obtained from our regular solution approach.

6. Conclusions

The results of this work can be summarised as follows:

1. The formation of a new phase in the quaternary Al–Fe–Mn–Si system has been confirmed by X-ray, microprobe and chemical analysis. There is a hope that this phase can be used to trap and remove iron from Al-based scraps. To learn about its power to bind iron, thermodynamic stability of this phase had to be assessed.

2. It has been demonstrated that despite its simplicity the regular solution model can provide useful information about activities in multicomponent alloys when used adroitly. Once the prediction is aimed at the calculations of activities in limited range of compositions this model is able to reproduce their values with great accuracy. In fact there is no big difference between suggested approach and results of calculations based on Thermocalc Database.

3. In turn one cannot expect better agreement if Thermocalc Database SSOL is used. It is not surprising that these values differ. When one takes a look at the data used for determination of the interaction parameter in Fe–Si system, it is clear that symmetric dependence of thermodynamic function represented by regular solution model cannot project $\ln \gamma_{Si}$ in liquid iron properly, due to asymmetry this system exhibits in reality. This is probably the main source of error since our parameters were fitted to $\ln \gamma_{Fe}$ data. Had the experimental data for activities of silicon in iron been available at iron-rich side of the system, the interaction parameter in this system used in our work would have got a different value. Recent evaluation of the iron-silicon system published by Schmid [26] shows clearly that partial functions of components in the liquid solutions are far from being symmetric. We suspect that this correction would reduce significantly the difference between calculated Gibbs free energies shown in Fig. 6.

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