Journal of Physics: Conference Series

Thermodynamic modelling of phase equilibria in melts of Fe-Ca-Al-Si-Mn-V-Nb-Ni-Mo-P-C-O system

Journal of Physics: Conference Series **98** (2008) 032014 doi:10.1088/1742-6596/98/3/032014

Thermodynamic modelling of phase equilibria in melts of Fe-Ca-Al-Si-Mn-V-Nb-Ni-Mo-P-C-O system

N M Tanklevskaya, L A Chernova and G G Mikhailov

South-Ural State University, 76 Lenin av., Chelyabinsk 454080, Russia

E-mail: nmt@fizchim.susu.ac.ru

Abstract. A thermodynamic analysis of the phase equilibria in the Fe-Ca-Al-Si-Mn-V-Nb-Ni-Mo-P-C-O system at fixed concentrations of silicon, manganese, vanadium, niobium, nickel, molybdenum, phosphorus and carbon was performed. The formation of nonmetallic phases at 1873 K in liquid metal solutions of various compositions was studied. It has been established that, depending on the concentrations of calcium and aluminum, the metal melt can be in equilibrium with (FeO, CaO, Al_2O_3, SiO_2, MnO) liquid solutions, |FeO, CaO, MnO| and |Al_2O_3, V_2O_3| solid solutions, individual compounds $3Al_2O_3{\cdot}SiO_2$, $CaO{\cdot}2Al_2O_3$, $CaO{\cdot}6Al_2O_3$ and {Ca} gas.

The problem of productions of alloys with the required properties is directly related with the understanding of alloy components interaction with an atmosphere, impurities, and refining additives. Besides, the thermodynamic analysis of reactions of heterogeneous phases formation from metal melt components allows one to establish a relation between the metal structure modification and the change of chemical and phase contents of forming gaseous and condensed non-metal phases.

In this connection, a considerable body of research data on thermodynamics of dissolved in liquid iron components interaction is generalized and systematized, and the correlated values database is compiled. With this database the phase equilibria mathematical modeling is made in systems structurally close to real melts.

In the frame of this work we performed a thermodynamic analysis of the of nonmetallic phases formation in iron-based melt containing calcium, aluminium, silicon, manganese, vanadium, niobium, nickel, molybdenum phosphorus, carbon and oxygen. The concentrations of some elements were fixed ([Si]=0.3; [Mn]=0.5; [V]=0.03; [Nb]=0.01; [Ni]=3.0; [Mo]=0.2; [P]=0.01; [C]=0.1 wt. %) while those of aluminum and calcium were varied. An analysis of the phase equilibria in particular system demonstrated that, depending on the concentrations of aluminum and calcium, the liquid melt can be in equilibrium with the (FeO, CaO, Al_2O_3, SiO_2, MnO) liquid solutions, |FeO, CaO, MnO| and |Al_2O_3, V_2O_3| solid solution, {Ca} gas and individual compounds $3Al_2O_3{\cdot}SiO_2$, $CaO{\cdot}2Al_2O_3$, $CaO{\cdot}6Al_2O_3$.

Table 1 lists the reactions that describing these equilibria and their thermodynamic characteristics.

The activities of the of the liquid metal solution components were calculated using the Wagner method in conjunction with the published parameters values of the pair interactions between the elements dissolved in liquid iron [1-5].

The activities of the liquid oxyde solution components were calculated using the approximation of a subregular ionic solution which takes into account dependence of a cation coordination number on the melt composition [2].

The activities of the solid solutions components in the region under consideration can be closely described in the approximation of a perfect molar solution.

When the liquid metal–$CaO\cdot 6Al_2O_3$–$(Al_2O_3, V_2O_3)_{s.s.}$ equilibrium is realized, the system under study (at eleven fixed parameters) will have three degrees of freedom.

Consequently, varying the concentration of one of the components, for example, calcium, and solving the equations for the equilibrium constants of reactions 9, 10 and 13 with consideration given to the data listed in Table 1 and the normalization conditions:

$$[Fe]+[Mn]+[Cr]+[Si]+[Al]+[Ti]+[C]+[N]+[O]=100\ \%; \quad (1)$$

$$x_{|Al_2O_3|s.s.} + x_{|V_2O_3|s.s.}, \quad (2)$$

(where $x_{|Al_2O_3|s.s.}$ and $x_{|V_2O_3|s.s.}$ is the component mole fraction in the solid solution), one can calculate the compositions of the coexisting phases at desired pressures and temperatures.

Table 1. Temperature dependences of the equilibrium constants for the reactions [1, 2] (l. – liquid; s. – solid; s.s. – solid solution; g. – gas)

Number	Reaction	$\lg K = -\frac{A}{T} + B$	
		A	B
1.	$(FeO)_{l.}=[Fe]+[O]$	6320	4.734
2.	$(CaO)_{l.}=[Ca]_l+[O]$	31480	12.55
3.	$(Al_2O_3)_l = 2[Al]_l +3[O]_l$	58320	18.02
4.	$(MnO)_l = [Mn] + [O]$	12175	5.45
5.	$(SiO_2)_l = [Si] + 2[O]$	30225	11.56
6.	$\|FeO\|_{s.s.}=[Fe]+[O]$	8069	5.8
7.	$\|CaO\|_{s.s.}=[Ca]+[O]$	34103	13.46
8.	$\|MnO\|_{s.s.}=[Mn]+[O]$	15017	6.77
9.	$\|Al_20_3\|_s = 2[Al] +3[0]$	64000	20.48
10.	$\|V_20_3\|_s = 2[V] +3[0]$	45430	18.62
11.	$\|CaO\cdot Al_20_3\|_{s.}=[Ca]+2[Al]+4[O]$	95304	31.06
12.	$\|CaO\cdot 2Al_20_3\|_{s.}=[Ca]+4[Al]+7[O]$	161775	52.34
13.	$\|CaO\cdot 6Al_20_3\|_{s.}=[Ca]+12[Al]+19[O]$	426169	138.03
14.	$\|\|SiO_2\|_{s.} = [Si] + 2[O]$	31100	12.0
15.	$\|3Al_20_3\cdot 2SiO_2\|_{s.}= 6[Al] + 2[Si]+ 13[O]$	257700	86.10
16.	$\{CO\}_g = [C] + [O]$	1168	– 2.07
17.	$\{CO_2\}_g = [C] + 2[O]$	9616	2.51
18.	$\{Ca\}_g= [Ca]$	– 1912	– 2.69

The calculation results were presented as isocompositional and isothermal sections of the surface of components solubility in the liquid metal solution of the system. Figure 1 shows the phase equilibrium in the liquid metal solution of the system under consideration at 1873 K presented in the lg[Ca]–lg[Al] coordinates at [Si] = 0.3; [Mn] = 0.5; [V] = 0.03; [Nb] = 0.01; [Ni] = 3.0; [Mo] = 0.2; [P] = 0.01; [C]=0.1 wt. %.

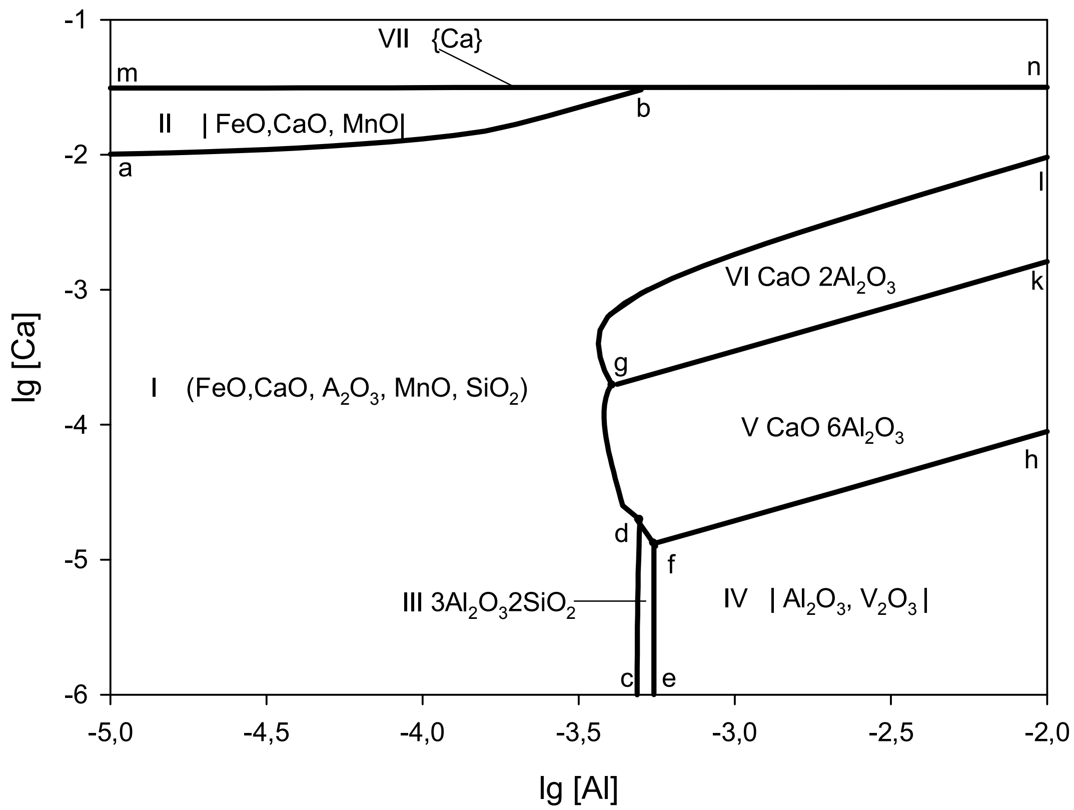

Figure 1. Phase equilibrium in the Fe–Ca–Al–Si(0.3)–Mn(0.5)–V(0.03)–
–Nb(0.01)–Ni (3.0)–Mo (0.2)–P (0.01)–C(0.1)-O system (in wt.%) at 1873 K.

Region I of the diagram plotted in figure 1 represents the melt composition in equilibrium with liquid oxide solutions of variable composition; region II – with (CaO, MnO, FeO) solid solutions of variable composition on a basis CaO; region III – with $3Al_20_3 \cdot 2SiO_2$, regions IV – with nearly pure corundum (Al_2O_3), regions V and VI – with $CaO \cdot 6Al_20_3$ and $CaO \cdot 2Al_20_3$ respectively, region VII – with gaseous calcium. Contrast lines correspond to liquid metal compositions in equilibrium with two nonmetallic phases. The line mn corresponds to limiting solubility of calcium in the liquid metal of the investigated system at 1873 K.

Conclusions

A thermodynamic analysis of the formation of nonmetallic phases in iron-based melt containing Ca, Al, Si, Mn, V, Nb, Ni, Mo, C, P and O has been made at the temperatures of existence of molten metal. The concentrations of some elements were fixed ([Si]=0.3; [Mn]=0.5; [V]=0.03; [Nb]=0.01; [Ni]=3.0; [Mo]=0.2; [P]=0.01; [C]=0.1 wt. %), while those of calcium and aluminum were varied.

An analysis of the phase equilibria in particular system demonstrated that, depending on the concentrations of calcium and aluminum, the liquid melt can be in equilibrium with the (FeO, CaO,

Al_2O_3, SiO_2, MnO) liquid solutions, |FeO, CaO, MnO| and |Al_2O_3, V_2O_3| solid solutions, {Ca} gas and individual compounds $3Al_2O_3 \cdot SiO_2$, $CaO \cdot 2Al_2O_3$, $CaO \cdot 6Al_2O_3$.

The area limits of the liquid metal composition being in equilibrium with a nonmetallic phase are determined.

Acknowledgements
The research has been carried out with the financial support of the Government of the Chelyabinsk region.

References

[1] Elliott J F, Gleiser M and Ramakrishna V 1963 *Thermochemistry for Steelmaking* (Addison–Wesley, Reading, Mass.)
[2] Michailov G and Povolotsky D 1993 *Thermodynamics of Steel Oxide* (Moscow: Metallurgy)
[3] 1988 *Steelmaking Data Sourcebook* (Gordon and Breach Science Publishers S.A.)
[4] Sigworth G K and Elliott J F 1974 *Met. Sci.* **31** 9
[5] Buzek Z 1979 *Hutnic Actuality* **1–2** 20