THERMODYNAMIC PROPERTIES
OF HETEROGENEOUS SYSTEMS

Thermodynamic Characteristics of the Interaction of Oxygen with Metal Melts of Fe–V–Me–Si–O–C (Me = Cr and Mn) Systems

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Abstract—Based on the thermodynamics of the oxidation of the individual dopants in liquid metal alloys and on the topology of the phase diagrams of the oxide systems conjugated with the liquid metal alloys, surfaces of solubility of components of liquid metals (state diagrams) were constructed; an analysis of the nature of phase equilibria at various compositions of liquid metal solutions of the Fe–V–Cr–Si–O–C and Fe–V–Mn–Si–O–C systems was performed.

At present, the body of accumulated experimental data on the interaction of oxygen dissolved in liquid metal melts with their components is large enough to make it possible to systematize information on the mechanisms of the formation of nonmetallic phases. The problem can be solved by constructing special phase diagrams in order to establish the relationship between the composition of the liquid metal and the feasibility of existence of various types of nonmetallic phases at equilibrium with the metal and to determine the changes in the phase equilibria caused by changes of the external conditions or the metal melt composition.

A change in the composition of a liquid metal solution by several thousandths of 1% may cause significant changes in the character of the equilibrium state. The composition of an equilibrium liquid metal solution is determined using a complex concentration surface of solubility of its components, with the composition of the conjugated nonmetallic equilibrium phases being calculated from another surface that corresponds to the state diagrams of oxide and other nonmetallic phases stable at the given temperature. The boundaries of the composition regions of the metal solution in equilibrium with various nonmetallic phases of constant and variable compositions are determined by jointly solving the equations for the equilibrium constants of the reactions that occur in the given system with respect to the concentrations of components of the metal and oxide phases, a procedure that determines the activities of the components as functions of the composition.

Based on binary and ternary phase diagrams, we performed a thermodynamic analysis of the interactions between oxygen, chromium, vanadium, silicon, and carbon in liquid iron. It was found that the following oxide phases can be in equilibrium with the liquid

metal: oxide melts 1 (high-iron) and 2 (high-silicon) that contain FeO, Cr_2O_3, V_2O_3, SiO_2, CrO, and VO; solid solutions of oxides $|Cr_2O_3, V_2O_3|$ and spinels $|FeV_2O_4, FeCr_2O_4|$ (s.s.sln); and solid SiO_2, VO, and Cr_3O_4 (the temperature dependences of the equilibrium constants are listed in Table 1). In the presence of carbon, gaseous CO and CO_2 can be formed.

Table 1. Temperature dependence of the equilibrium constants ($\log K = -A/T + B$)

Reaction	A	B
$(FeO) = [Fe] + [O]$	6320	4.734
$(SiO_2) = [Si] + 2[O]$	30225	11.56
$(Cr_2O_3) = 2[Cr] + 3[O]$	33460	14.85
$(V_2O_3) = 2[V] + 3[O]$	39303	15.90
$(MnO) = [Mn] + [O]$	12175	5.45
$(CrO) = [Cr] + [O]$	8203	4.51
$(VO) = [V] + [O]$	11760	5.06
$|FeO| = [Fe] + [O]$	8069	5.80
$|MnO| = [Mn] + [O]$	15017	6.77
$|FeV_2O_4| = [Fe] + 2[V] + 4[O]$	58522	26.48
$|MnV_2O_4| = [Mn] + 2[V] + 4[O]$	66087	27.76
$|FeCr_2O_4| = [Fe] + 2[Cr] + 4[O]$	51870	24.48
$|MnCr_2O_4| = [Mn] + 2[Cr] + 4[O]$	55600	24.19
$|SiO_2| = [Si] + 2[O]$	31100	12.00
$|Cr_2O_3| = 2[Cr] + 3[O]$	40014	17.37
$|V_2O_3| = 2[V] + 3[O]$	45430	18.617
$|Cr_3O_4| = 3[Cr] + 4[O]$	53352	23.51
$|VO| = [V] + [O]$	15040	6.453
$\{CO\} = [C] + [O]$	1168	–2.07
$\{CO_2\} = [C] + 2[O]$	9616	2.51

Note: Designation: (), the oxide melt; [ ], liquid metal phase; | |, crystalline state; and { }, gas phase.

Table 2. Energy parameters of the theory of subregular ionic solutions for $FeO-V_2O_3-Cr_2O_3-SiO_2-MnO$ oxide melts [2, 3]

System	Q_{ijkl}, J/mol		
$FeO-V_2O_3$	$Q_{1112} = 14650$	$Q_{1122} = 25100$	$Q_{1222} = 23000$
$FeO-Cr_2O_3$	$Q_{1113} = 4360$	$Q_{1133} = 26700$	$Q_{1333} = 5400$
$FeO-SiO_2$	$Q_{1114} = 960$	$Q_{1144} = -34100$	$Q_{1444} = 50500$
$FeO-MnO$	$Q_{1115} = 0$	$Q_{1155} = 0$	$Q_{1555} = 0$
$V_2O_3-Cr_2O_3$	$Q_{2223} = 17150$	$Q_{2233} = 34300$	$Q_{2333} = 17150$
$V_2O_3-SiO_2$	$Q_{2224} = 71150$	$Q_{2244} = 142300$	$Q_{2444} = 71150$
V_2O_3-MnO	$Q_{2225} = 0$	$Q_{2255} = 0$	$Q_{2555} = 0$
$Cr_2O_3-SiO_2$	$Q_{3334} = 49950$	$Q_{3344} = 83500$	$Q_{3444} = 64200$
Cr_2O_3-MnO	$Q_{3335} = 0$	$Q_{3355} = 0$	$Q_{3555} = 0$
SiO_2-MnO	$Q_{4445} = 36800$	$Q_{4455} = -85100$	$Q_{4555} = -7400$
$FeO-V_2O_3-Cr_2O_3$	$Q_{1123} = 62800$	$Q_{1223} = 79500$	$Q_{1233} = 77600$
$FeO-V_2O_3-SiO_2$	$Q_{1124} = 230200$	$Q_{1224} = 418500$	$Q_{1244} = 376650$
$FeO-V_2O_3-MnO$	$Q_{1125} = 0$	$Q_{1225} = 0$	$Q_{1255} = 0$
$FeO-Cr_2O_3-SiO_2$	$Q_{1134} = 50200$	$Q_{1334} = 113000$	$Q_{1344} = 146500$
$FeO-Cr_2O_3-MnO$	$Q_{1135} = 0$	$Q_{1335} = 0$	$Q_{1355} = 0$
$FeO-SiO_2-MnO$	$Q_{1145} = 83700$	$Q_{1445} = 125550$	$Q_{1455} = 104650$
$V_2O_3-Cr_2O_3-SiO_2$	$Q_{2234} = 0$	$Q_{2334} = 0$	$Q_{2344} = 376650$
$V_2O_3-Cr_2O_3-MnO$	$Q_{2235} = 0$	$Q_{2335} = 0$	$Q_{2355} = 0$
$V_2O_3-SiO_2-MnO$	$Q_{2245} = 209250$	$Q_{2445} = -418500$	$Q_{2455} = 334800$
$Cr_2O_3-SiO_2-MnO$	$Q_{3345} = 0$	$Q_{3445} = 0$	$Q_{3455} = 0$

Table 3. Parameters of interaction e_i^j of the components in the liquid metal solution at $T = 1873$ K

Element i	Element j					
	Si	Mn	V	Cr	O	C
Si	0.14	0.03	0.025	−0.0003	−0.176	0.187
Mn	0.06	0	0.0057	0.0039	−0.072	−0.055
V	0.0425	0.0053	0.015	0	−0.534	−0.327
Cr	−0.0006	0.0037	0	−0.0003	−0.133	−0.104
O	−0.1	−0.021	−0.168	−0.041	−0.2	−0.45
C	0.08	−0.012	−0.077	−0.024	−0.34	0.14
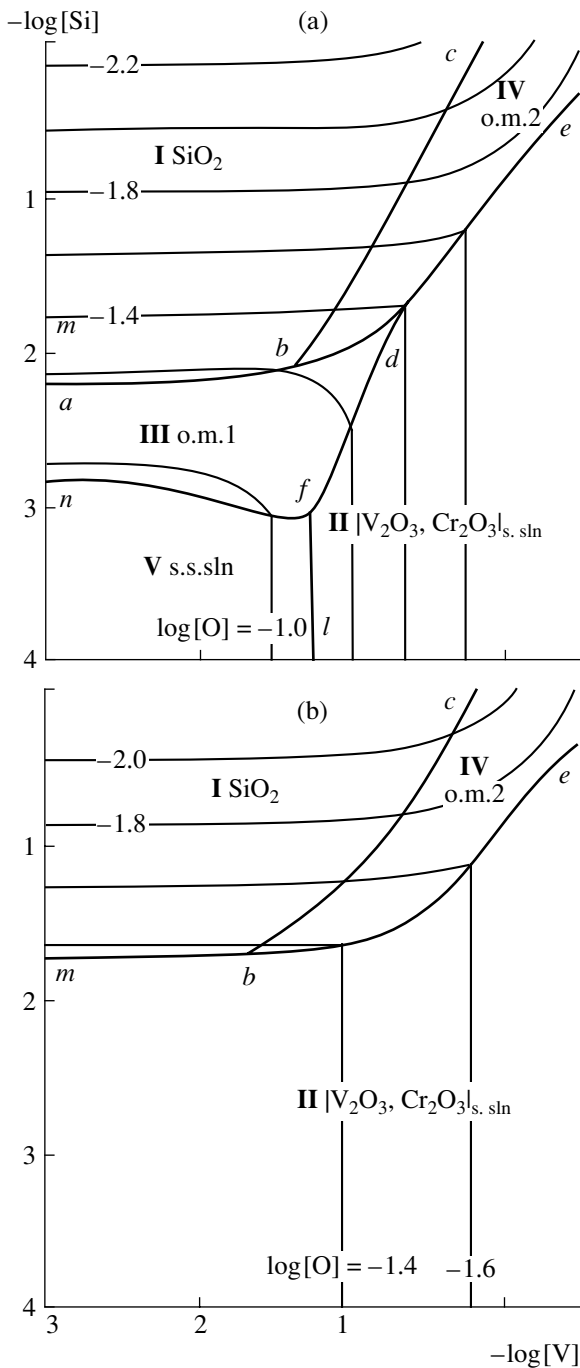
Fig. 1. SSMC section of the Fe–V–Cr–Si–O system at T = 1873 K; [Cr] = (a) 0.25 and (b) 1.5 wt %.

Fig. 2. SSMC section of the Fe–V–Cr–Si–O–C system at T = 1873 K; [Cr] = 1.5 wt %, [C] = 0.2 wt %, p_{tot} = 1 atm.

The activities of the components of the solid solution of $|Cr_2O_3, V_2O_3|$ were calculated within the framework of the theory of regular solutions (Q_{12} = 16740 J/mol). The activity of components of the oxide melt (FeO, Cr_2O_3, V_2O_3, and SiO_2) were calculated based on the theory of subregular ionic solutions. The general formula for calculating the activity of the component s in the oxide melt reads as [1]
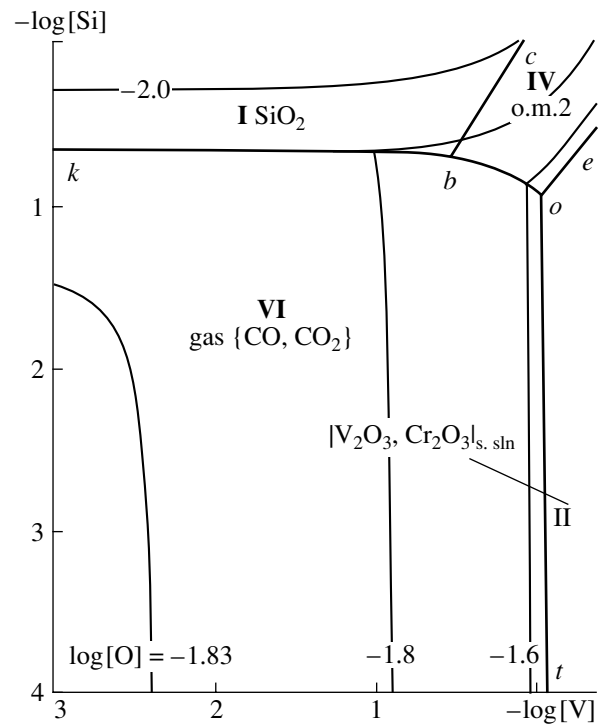
$$RT\ln a_s = v_s \Bigg[RT\ln x_s$$

$$+ \sum_{i=1}^{s-1} (x_i^3 Q_{iiis} + 2x_i^2 x_s Q_{iiss} + 3x_i x_s^2 Q_{isss})$$

$$+ \sum_{j=s+1}^{m} (3x_s^2 x_j Q_{sssj} + 2x_s x_j^2 Q_{ssjj} + x_j^3 Q_{sjjj})$$

$$- 3\sum_{i=1}^{m-1} \sum_{j=i+1}^{m} (x_i^3 x_j Q_{iiij} + x_i^2 x_j^2 Q_{iijj} + x_i x_j^3 Q_{ijjj})$$

$$+ \sum_{i=1}^{s-2} \sum_{j=i+1}^{s-1} (x_i^2 x_j Q_{iijs} + x_i x_j^2 Q_{ijjs} + 2x_i x_j x_s Q_{ijss})$$

$$+ \sum_{i=1}^{s-1} \sum_{k=s+1}^{m} (x_i^2 x_k Q_{iisk} + 2x_i x_s x_k Q_{issk} + x_i x_k^2 Q_{iskk})$$

$$+ \sum_{j=s+1}^{m-1} \sum_{k=s+2}^{m} (2x_s x_j x_k Q_{ssjk} + x_j^2 x_k Q_{sjjk} + x_j x_k^2 Q_{sjkk})$$

$$-3\sum_{i=1}^{m-2}\sum_{j=i+1}^{m-1}\sum_{k=i+2}^{m}(x_i^2 x_j x_k Q_{iijk}+x_i x_j^2 x_k Q_{ijjk}$$

$$+x_i x_j x_k^2 Q_{ijkk})+\sum_{i=1}^{s-3}\sum_{j=i+1}^{s-2}\sum_{k=j+1}^{s-1}x_i x_j x_k Q_{ijks}$$

$$+\sum_{i=1}^{s-2}\sum_{j=i+1}^{s-1}\sum_{k=s+1}^{m}x_i x_j x_l Q_{ijsl}$$

$$+\sum_{i=1}^{s-1}\sum_{k=s+1}^{m-1}\sum_{l=k+1}^{m}x_i x_k x_l Q_{iskl}$$

$$+\sum_{j=s+1}^{m-2}\sum_{k=j+1}^{m-1}\sum_{l=k+1}^{m}x_j x_k x_l Q_{sjkl}$$

$$\left.-\sum_{i=1}^{m-3}\sum_{j=i+1}^{m-2}\sum_{k=j+1}^{m-1}\sum_{l=k+1}^{m}x_i x_j x_k x_l Q_{ijkl}\right].$$

Here, x_i are the ionic fractions of the cations of the slag melt components and Q_{ijkl} are the energy parameters. The calculations employ only part of the general formula, with the number indices in Q_{ijkl} not exceeding three.

The adjusted energy parameters of the theory of subregular ionic solutions are listed in Table 2. Because of the absence of reliable literature data on state diagrams for systems containing CrO and VO, their activities were set equal to their ionic fractions (in accordance with the theory of ideal ionic solutions). The activity of the components of the metal melts was calculated in terms of the Wagner theory with the use of the interaction parameters listed in Table 3.

We constructed the surfaces of solubility of liquid metal components (SSMC) for the Fe–V–Cr–Si–O system. We studied the effects of the temperature and contents of carbon and chromium or vanadium on the SSMC structure. Figures 1 and 2 show the isothermal isocomposition sections of SSMC for the Fe–V–Cr–Si–O system at $T = 1873$ K. Region **I** encompasses compositions of liquid metal solutions in equilibrium with silicon; region **II**, solid solutions of trivalent vanadium and chromium; region **III**, the high-iron oxide melt (o.m.1); section **IV**, the high-silicon oxide melt (o.m.2); section **V**, the solid solution of spinel (s.s.sln); and section **VI**, gaseous CO and CO_2. The isooxygen sections of SSMC are shown by thin lines.

The content of vanadium in steels is typically a few tenths of 1%, while the content of chromium in many steels is ~1.5 wt %. At these concentrations, the probability of formation of a solid solution of trivalent vanadium and chromium oxides and practically pure liquid SiO_2 at equilibrium with liquid metal is very high.
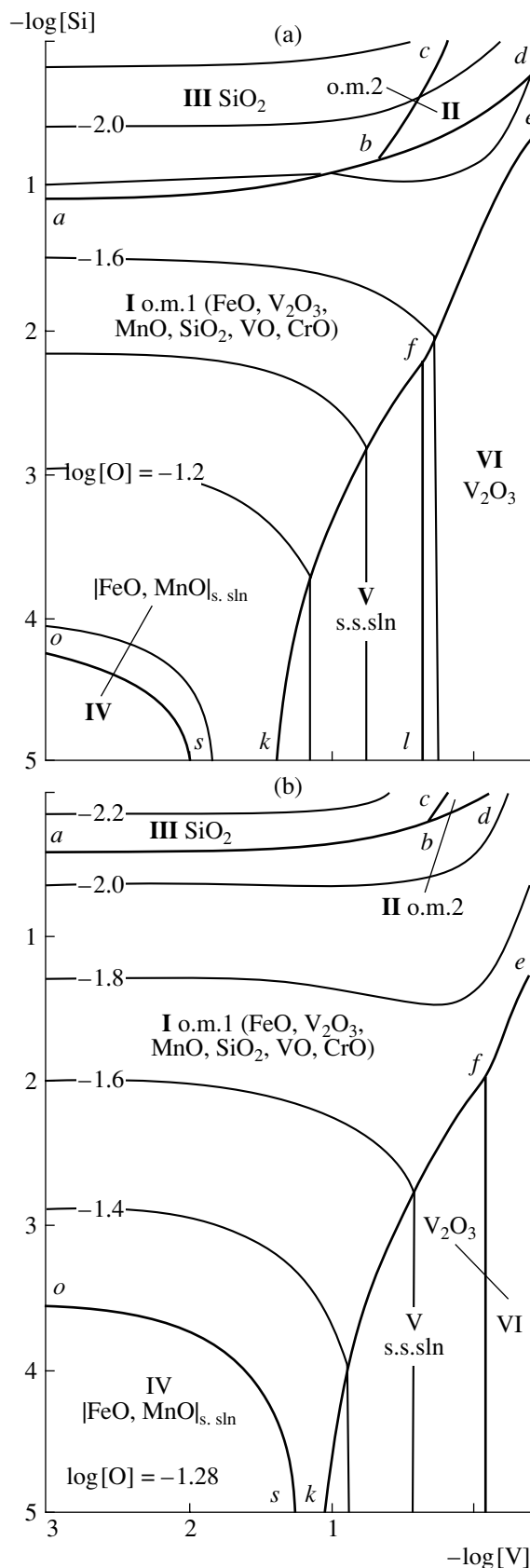

Fig. 3. SSMC section of the Fe–V–Mn–Si–O system at $T = 1873$ K; (a) [Mn] = 0.4 and (b) 1 wt %.

Solid SiO_2 may be at equilibrium with the liquid metal solution only if the vanadium concentration does not exceed 0.3 wt % and the chromium content is 1.5 wt %. If the chromium content in liquid metal is higher than 10 wt %, Cr_3O_4 can be formed; at vanadium concentrations in the metal solution above 8 wt %, VO can be formed.

We also studied the effect of temperature and the composition of the liquid metal on the formation of nonmetallic phases at equilibrium with the liquid metal solution in the Fe–V–Mn–Si–O system. Figure 3 shows the isothermal isocomposition sections of SSMC of the Fe–V–Mn–Si–O system at various manganese contents. The initial data for calculating SSMC are listed in Tables 1–3. The activities of the components of solid solutions of FeO and MnO and the FeV_2O_4 and MnV_2O_4 spinels were set equal to the corresponding mole fractions (in accordance with the theory of ideal solutions). Manganese is added to vanadium-containing metals in amounts 0.4–1.0 wt %, whereas the content of silicon is typically tenths of 1%. At these concentrations, the probability of formation of liquid non-metallic phases and trivalent vanadium oxide (at low manganese content) at equilibrium with the liquid metal solution is very high. A similar picture is observed in the presence of carbon if its concentration does not exceed 0.2 wt %.

The proposed method for analyzing equilibria between liquid metals and nonmetallic phases makes it possible to develop technologies of refining liquid metals by removing oxygen and to model the phase equilibria involved.

REFERENCES

1. E. M. Vil'gel'm and G. G. Mikhailov, in *Physicochemical Studies of Metallurgical Processes: A Collection of Papers* (Izd. Ural'sk. Politekhn. Inst., Sverdlovsk, 1978), pp. 63–69 [in Russian].

2. G. G. Mikhailov and L. A. Chernova, Izv. Vyssh. Uchebn. Zaved., Chern. Metall., No. 12, 37 (1991).

3. G. G. Mikhailov and L. A. Chernova, in *Computer Simulation of Physicochemical Properties of Glasses and Melts: Proceedings of VII Russian Seminar* (Izd. Kurgansk. Univ., Kurgan, 2004), pp. 41–43.