



Calculation of phase equilibrium in Fe-B-C-O system

K. Lenik ^a, M. Pashechko ^{a, b *}, A. Kondyr ^b, L. Bohun ^b, Z. Lenik ^a

^a Education Technical and Information Department of Lublin University,
ul. Nadbystrzycka 38, Lublin 20-618, Poland

^b Lviv Politechnic National University, 13 Bandera str., Lviv 79013, Ukraine

* Corresponding author: E-mail address: pashechko@hotmail.com

Received 20.04.2007; published in revised form 01.08.2007

ABSTRACT

Purpose: This paper presents calculation of phase equilibrium in Fe-B-C-O system.

Design/methodology/approach: The typical phase equilibrium diagrams do not always provide useful information on this problem, especially for polycomponent systems. Instead of this, the methods for phase equilibrium calculations, the necessary data about thermodynamic properties of agents being available, can simplify greatly the problem of prediction of the composition of the oxide layer and accelerate its solution.

Findings: In order to predict the phase composition of the boron-carbon surface layers during surfacing as well as of the secondary structures under wear, the calculations of the phase equilibrium in Fe-B-C-O system at 723, 843 and 1644 K have been carried out.

Research limitations/implications: The phase equilibrium calculations in the friction couples, containing boron and carbon agree well with the results of investigations of the chemical and phase composition of the secondary structures of wear, formed during friction of boron and carbon-containing composites.

Originality/value: The carbon concentration increases on the contact surface. This is caused, in our opinion, by the graphite film formation due to carbon monoxide stability. The boron content in the composition of wear products increases as a result of melting and formation of the oxide layer on the friction surface.

Keywords: Calculation; Phase equilibrium; Fe-B-C-O system

PROPERTIES

1. Introduction

The boron-carbon coatings exhibit good tribological properties: the low coefficient of friction and the low degree of wear. This is explained by formation of the interlayer of a liquid phase; boron oxide, in the friction couple [1, 2]. The oxide films on the metal are also very important for different processes, taking place on the surface of solids. The positive effect of the oxide layers under friction and wear consists in the substantial decrease in the monomolecular interaction forces on the friction surface. The efficiency of some lubricants is considered to be worse while operating in the oxygen-free environment [1].

The strength of the oxide film adhesion with metals, their continuity and the influence of the microrelief of the friction surface, depend significantly on the phase composition of the surface layer. However, it is a complex and in some cases cost-effective task to establish experimentally the phase composition of the surface layer. The information about the surface phase composition when applying composite materials, e. g. surfacing, is useful too. The typical diagrams of the state do not always provide useful information on this problem, especially for polycomponent systems. Instead of this, the methods for phase equilibrium calculations, the necessary data about thermodynamic properties of agents being available, can simplify greatly the problem of prediction of the composition of the oxide layer and accelerate its solution.

By using the researches into the phase equilibrium in B-C-O and Fe-C-O systems and also the secondary structure composition, the agreement between the results of thermodynamic calculations and experimental investigation of the oxide composition of B₄C friction against IIX15 steel has been shown in [3].

A good correlation between the calculated and experimental data on phase equilibrium in the model three-component B-C-O and Fe-C-O alloys allows us to make the analysis of the equilibrium conditions in a more complex system Fe-B-C-O.

2. Experiment

This paper is aimed at the development of the methods for prediction of the composition of the secondary structures of wear by plotting the phase equilibrium diagrams for the given temperatures, that were chosen in dependence of the peculiarities of the physico chemical processes taking place on the friction surfaces.

The eutectic coatings of Fe-B-C system, applied by plasma spraying were chosen as the model alloys. The structure of the contact surfaces and the secondary structure compositions were studied by the methods given in [3]. For the thermodynamic calculations the data on the enthalpy of compounds formations and temporal dependence of the change of free energy of simple reactions have been used [4, 5].

The phase composition of boron-carbon-containing coatings has been investigated elsewhere [2, 6, 7]. In the majority of cases the coatings consist of carbon borides in which, depending on chemical composition of the coating, Mn and Cr can also dissolve. Since there were no adequate thermodynamic data, the calculations were carried out assuming that in the first approximation the coatings consisted of Fe₃C, Fe₂B and FeB. The analysis of the published data testifies to the fact that on the contact friction surfaces, the temperature is distributed in the wide range [1, 8, 9]. In a general case we speak about the physicochemical processes that can lead to significant concentration of thermal energy in some sites of contact. As a result the temperature of the individual sources of thermal energy during friction can attain the melting temperature of one of the bodies in the contact couple [1, 8]. The topological peculiarities of the contact surface construction — the presence of the doomed films and almost spherical shape of the wear particles in the friction couple B₄C – IIX15 steel — are, in our opinion, the feature of the secondary phases melting [1, 3, 10]. Among the phases that are formed during oxidizing wear of this friction couple, boron oxide has the lowest softening temperature—450 °C.

3. Results

So, the value of such an order can be one of the typical temperatures in friction contact. However, the presence of the spherical particles on the boron carbide surface proves that the maximum temperature of the single spot of actual contact is much higher and sufficient to cause the significant decrease in temperature and to give the oxide particles the spherical shape. Thus, the material of the most loaded local regions of friction contact is subjected to a short-term effect of high temperature,

resulting from the influence of chemical reactions on the heat formation process on the sliding surfaces. The calculation results (Table 1) illustrate that the thermal effect of the reaction of phase oxidation in friction couples is sufficiently high to cause the significant increase in temperature in certain highly-loaded sites of actual contact.

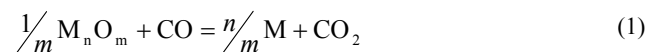
When considering the chemical reaction, participating in formation of the phase composition of the secondary structures, it must be noted that during friction the gaseous mixture is formed. Its main components are mono- and dioxide of carbon and, in our opinion, this mixture plays an important role in the physicochemical processes under contact interaction.

Therefore, the phase composition of oxide systems was determined by thermodynamic analysis of the conditions of the reactions, taking place with participation of mono- and dioxide of carbon. The equilibrium calculations in the Fe-B-C-O system have been performed according to the equations of reactions, and temporal dependences of their free energy as well as a constant of equilibrium (see Table 2).

Here and hereafter the square brackets the French brackets, and parenthesis designate the solid, liquid and gaseous state of the agent.

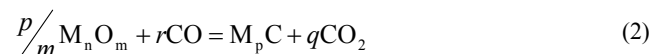
In our opinion the apriori critical temperature that is to be accounted when analyzing the process of oxidizing wear of the materials, containing iron, does not exceed the point of melting (softening) of the most easily melted iron oxide Fe₂O₃, i.e. 1391 °C. By using the above mentioned, the calculations of the phase composition of the secondary structures were carried out at temperatures typical of the investigated physicochemical systems, namely at 723, 843 and 1644 K. The first temperature was chosen because several independent researches showed that during friction of boron coatings or ceramic materials based on boron, the friction characteristics change i due to formation of B₂O₃ and its melting at 723 K [1, 2, 10]. The second temperature corresponds to the change of the course of reactions in the Fe-C-O system from a two-stage to a three-stage process [11]. The third one is considered as a temperature of contact (according to Bloch) that also corresponds to the point of melting of Fe_{0,947}O.

Among those considered, the reactions metal-oxide or higher-lower oxides proceed at the equal number of moles of mono- and dioxide of carbon:



where M is the chemical element that forms oxide.

The reactions involving carbides and borides, are characterized by a different number of moles of the gas-reagent and the gas-product, as e.g. in the simplest case for carbides (see Table 2).



Under the above condition for condensed phases where the constant of equilibrium of reaction (2) was determined from the equation:

$$K_p = \frac{p_{CO_2}^q}{p_{CO}^r} \quad (3)$$

Table 1.

A standard enthalpy of chemical oxidation reaction that form the phase composition of the secondary structures of Fe-B-C materials

	Reaction equation	ΔH_{298}^0 , KJ/mol	Error, KJ/mol ⁻¹
1.	$\frac{2}{7} B_4C + O_2 = \frac{4}{7} B_2O_3 + \frac{2}{7} CO$	-731,1	± 18,5
2.	$\frac{1}{4} B_4C + O_2 = \frac{1}{2} B_2O_3 + \frac{1}{4} CO_2$	-719,6	± 16,2
3.	$\frac{4}{11} Fe_3C + O_2 = \frac{6}{11} Fe_2O_3 + \frac{4}{11} CO$	-496,9	± 4,1
4.	$\frac{4}{13} Fe_3C + O_2 = \frac{6}{13} Fe_2O_3 + \frac{4}{13} CO_2$	-507,5	± 3,5
5.	$\frac{4}{9} Fe_2B + O_2 = \frac{4}{9} Fe_2O_3 + \frac{2}{9} B_2O_3$	-650,2	± 14,9
6.	$\frac{2}{3} FeB + O_2 = \frac{1}{3} Fe_2O_3 + \frac{1}{3} B_2O_3$	-648,2	± 14,3
7.	$2CO + O_2 = 2CO_2$	-565,96	± 0,28

Table 2.

Temporal dependence of the change of Gibb's free energy and a constant of the equilibrium of equations in the Fe-B-C-O system

№	Reaction equation	ΔG_T^0 , J·mol ⁻¹	lg K_p
1.	$2(CO) = \langle C \rangle + (CO_2)$	$-166680 + 171,10T$	$8706/T - 8,93$
2.	$\{B_2O_3\} + 3(CO) = 2\langle B \rangle + 3(CO_2)$	$386232 + 45,68T$	$-20174/T - 2,39$
3.	$2\{B_2O_3\} + 8(CO) = \langle B_4C \rangle + 7(CO_2)$	$564255 + 268,04T$	$-29473/T - 14,00$
4.	$4\langle B \rangle + 2(CO) = \langle B_4C \rangle + (CO_2)$	$-208210 + 176,68T$	$10870/T - 9,23$
5.	$3\langle Fe_2O_3 \rangle + (CO) = 2\langle Fe_3O_4 \rangle + (CO_2)$	$-42810 - 52,08T$	$2246/T + 2,72$
6.	$\langle Fe_3O_4 \rangle + 4(CO) = 3\langle Fe \rangle + 4(CO_2)$	$-21748 + 33,80T$	$284/T - 0,44$
7.1.	$1,202\langle Fe_3O_4 \rangle + (CO) = 3,808\langle Fe_{0,947}O \rangle + (CO_2)$	$39670 - 39,19T$	$-2072/T + 2,05$
7.2.	$\langle Fe_3O_4 \rangle + (CO) = 3\{FeO\} + (CO_2)$	$159086 - 111,53T$	$-8310/T + 5,82$
8.1.	$\langle Fe_{0,947}O \rangle + (CO) = 0,947\langle Fe \rangle + (CO_2)$	$-17250 + 20,89T$	$901/T - 1,09$
8.2.	$\{FeO\} + (CO) = \langle Fe \rangle + (CO_2)$	$-48609 + 39,90T$	$2539/T - 2,08$
9.	$3\langle Fe \rangle + 2(CO) = \langle Fe_3C \rangle + (CO_2)$	$-137560 + 143,07T$	$7185/T - 7,47$
10.	$\langle Fe_3O_4 \rangle + 6(CO) = \langle Fe_3C \rangle + 5(CO_2)$	$-159266 + 176,60T$	$8319/T - 9,23$
11.1.	$3\langle Fe_{0,947}O \rangle + 4,894(CO) = 0,947\langle Fe_3C \rangle + 3,947(CO_2)$	$-174241 + 190,00T$	$9101/T - 9,92$
11.2.	$3\{FeO\} + 5(CO) = \langle Fe_3C \rangle + 4(CO_2)$	$-268319 + 247,15T$	$14015/T - 12,90$
12.	$\{B_2O_3\} + 2\langle Fe \rangle + 3(CO) = 2\langle FeB \rangle + 3(CO_2)$	$227134 + 66,6T$	$-11864/T + 3,47$
13.	$3\{B_2O_3\} + 2\langle Fe_3C \rangle + 5(CO) = 6\langle FeB \rangle + 7(CO_2)$	$960410 - 86,30T$	$-50165/T + 4,50$
14.	$12\langle FeB \rangle + 14(CO) = 3\langle B_4C \rangle + 4\langle Fe_3C \rangle + 7(CO_2)$	$-228055 + 976,70T$	$11912/T - 51,02$
15.	$\{B_2O_3\} + 4\langle Fe \rangle + 3(CO) = 2\langle Fe_2B \rangle + 3(CO_2)$	$210387 + 82,52T$	$-10989/T - 4,30$
16.	$3\{B_2O_3\} + 4\langle Fe_3C \rangle + (CO) = 6\langle Fe_2B \rangle + 5(CO_2)$	$1181641 - 324,69T$	$-61721/T + 16,96$
17.	$12\langle Fe_2B \rangle + 22(CO) = 3\langle B_4C \rangle + 8\langle Fe_3C \rangle + 11(CO_2)$	$-670516 + 1453,5T$	$35023/T - 75,92$

The temporal dependence of the constant of equilibrium was evaluated by the change of the reaction free energy, using the known equations:

$$\lg K_p = -\frac{\Delta G^0}{2,302RT} \quad (4)$$

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \quad (5)$$

By taking logarithm of (3) and substituting equation (5) into equation (4), after transformation we get:

$$q \lg p_{\text{CO}_2} - r \lg p_{\text{CO}} = -\frac{\Delta H^0}{2,302RT} + \frac{\Delta S^0}{2,302R} \quad (6)$$

The regressive analyseis used for experimental results processing [5] allows us to linearize equality (5) by describing it with equation:

$$\Delta G^0 = \Delta \tilde{H}^0 - T \Delta \tilde{S}^0 \quad (7)$$

Where ΔH and ΔS are the average values of enthalpy and entropy in the temperature range between the point of phase transformations of the reagents and the products of reaction.

In this case equality (6) is written as:

$$q \lg p_{\text{CO}_2} - r \lg p_{\text{CO}} = -\frac{\Delta \tilde{H}^0}{2,302RT} + \frac{\Delta \tilde{S}^0}{2,302R} \quad (6)$$

and the condition of stability of ΔH and ΔS is fulfilled.

The usage of this equation with imposing restrictions in order to establish the phase equilibrium in such a complex system as Fe-B-C-O is quite reasonable, since the similar analysis is very approximate. By imposing the condition of the stability temperature and one of the values of partial gas pressure, the diagram of state was constructed in coordinates $\lg p_{\text{CO}} - \lg p_{\text{CO}_2}$.

The results of phase equilibrium calculations (Fig.1) show that in the wide range of partial pressures of CO and CO₂, the oxidizing mechanism of wear of the boron-carbon-containing coatings prevails. The most probable temperature for this mechanism course is 723 K. At this temperature in the secondary structure composition, irrespective of the total pressure in the system, can prevail liquid B₂O₃ and Fe₂O₃ as well as Fe₃O₄. The boron and iron oxide can form borates 3Fe₂O₃·B₂O₃(Fe₃BO₆) and Fe₂O₃·B₂O₃(FeBO₃) relatively easy. Iron and boride are stable at very high ratios of CO/CO₂ in the gaseous mixture composition only. In the wide range of pressures CO proves to be unstable and is decomposed with formation of graphite and carbon dioxide [12]. Nonstability of cementite is caused by instability of the gas-reducer the gaseous mixture composition, the iron and the cementite can from the contact surface, while the increase in the pressure promotes their stabilization.

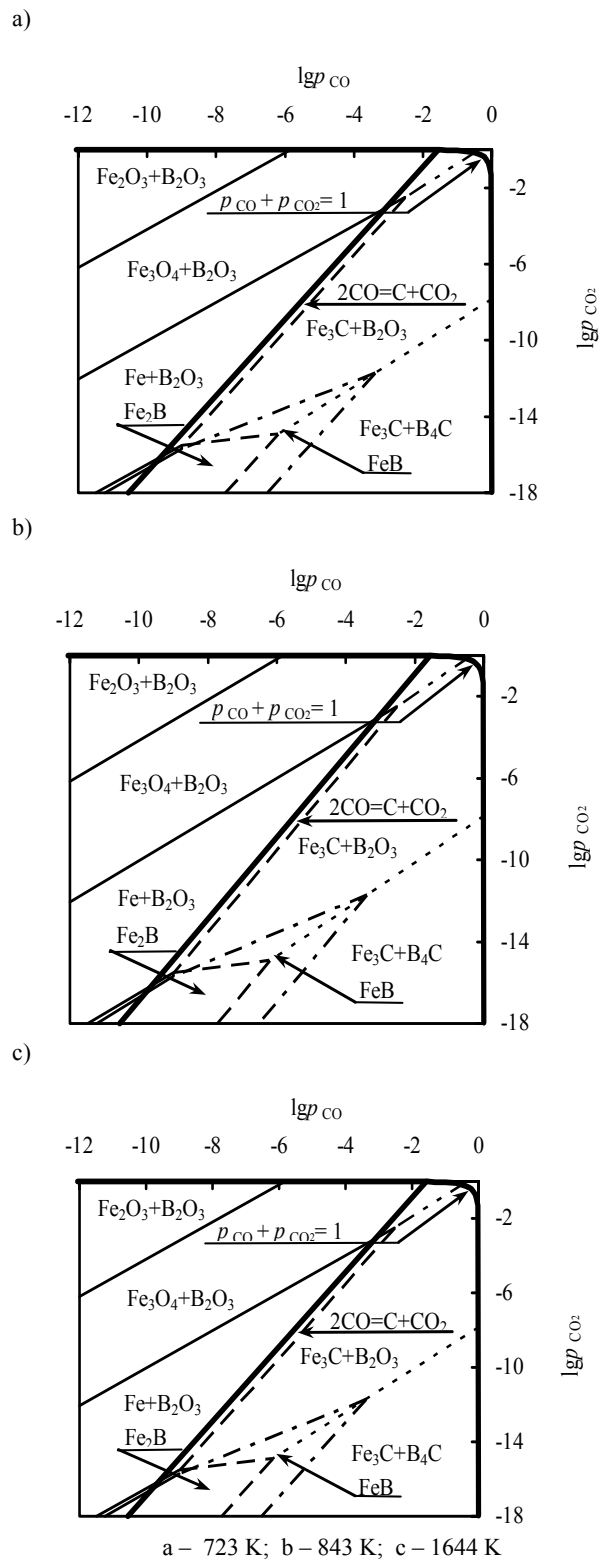


Fig. 1. Dual-phase equilibrium in Fe-B-C-O system at different temperatures

Table 3.
Chemical composition of the coating and friction surface during wear of over layer

Eutectic powder layer	Content of chemical elements, $\frac{wt\%}{at\%}$									
	Fe	Mn	C	B	Si	Ni	Cr	Al	Sc	O
Coatings										
Fe-Mn-C-B- Si-Ni-Cr-Al-Sc	<u>60.6</u>	<u>9.4</u>	<u>0.8</u>	<u>2.7</u>	<u>2.3</u>	<u>10.4</u>	<u>12.5</u>	<u>1.2</u>	<u>0.04</u>	—
	70.6	—	2.4	8.8	3.0	6.3	8.9	—	—	—
Fe-Mn-C-B- Si-Ni-Al-Sc	<u>62.7</u>	<u>7.3</u>	<u>0.3</u>	<u>3.8</u>	<u>2.8</u>	<u>22.0</u>	—	<u>1.1</u>	<u>0.04</u>	—
	68.9	—	3.8	11.6	3.3	12.4	—	—	—	—
Fe-Mn-C-B- Si-Cr-Al-Sc	<u>77.4</u>	<u>5.5</u>	<u>0.9</u>	<u>3.6</u>	<u>2.0</u>	—	<u>9.7</u>	<u>0.9</u>	<u>0.05</u>	—
	72.6	—	10.1	9.7	2.1	—	5.5	—	—	—
Friction surface										
Fe-Mn-C-B- Si-Ni-Cr-Al-Sc	<u>65.3</u>	—	<u>0.9</u>	<u>10.1</u>	<u>8.8</u>	<u>10.6</u>	<u>3.8</u>	—	—	<u>0.5</u>
	42.4	—	2.7	33.0	11.4	6.5	2.7	—	—	1.3
Fe-Mn-C-B- Si-Ni-Al-Sc	<u>59.3</u>	—	<u>0.7</u>	<u>8.4</u>	<u>13.3</u>	<u>15.6</u>	—	—	—	<u>2.7</u>
	35.4	—	8.6	25.6	15.8	8.8	—	—	—	5.8
Fe-Mn-C-B- Si-Cr-Al-Sc	<u>63.1</u>	—	<u>1.1</u>	<u>12.0</u>	<u>13.5</u>	—	<u>9.3</u>	—	—	<u>1.0</u>
	34.8	—	12.3	32.4	14.3	—	5.3	—	—	1.9

4. Discussion

The results of calculations were compared with the chemical composition of the coating and the friction surface after wear of the overlayer. They are presented in Table 3. Note that the results for more complex eutectic compositions are given here, however their phase composition can be considered approximately the same as in the triple system.

Here the following should be noted:

- The hydrogen concentration increases on the contact surface (in some cases more than 2-fold). This is caused, in our opinion, by the graphite film formation due to carbon monoxide stability;
- The boron content in the composition of wear products increases as a result of melting and formation of the oxide layer on the friction surface.

The obtained results concerning the phase equilibrium in the friction couples, containing boron and carbon agree well with published data [1, 3, 10] on the chemical and phase content of the products of wear.

References

- [1] B. Bakli Surface phenomena during adhesion and friction interaction, English-Moscow, Mashinostroyeniye Published House, 1986.
- [2] L.G. Voroshnin, V.F. Labunets Wear-resistant boron coatings-Kyiv, Technica Published House, 1989.
- [3] M. Pashechko, A. Kondyr, L. Bohun, Phase composition of wear products on the surface of friction pair B4C-III15 steei, Herald of State University Lviv Polytechnic 359 (1999) 77-83 (in Russian).
- [4] D.R. Stull, H. Prophet et al. JANAF Thermochemical Tables, 2nd edition, United States Department of Commerce, Document NSRDS – NBS 37, Washington, 1971.
- [5] E.T. Turkdogan Physical Chemistry of High Temperature Technology, New-York, Academic Press, 1980.
- [6] M.I. Pashechko, V.M. Holubets M.V. Chernets Formation and friction resistance of eutectic coatings, Kiev, Naukova Dumka Published House, 1993 (in Russian).
- [7] V.V. Drobit, V.F. Staninskyi, A.I. Kondyr The influence of the system saturating solution-basic material on the diffusion coatings parameters, Physicochemical Mechanics of Materials 5(1988) 28-32 (in Russian).

- [8] P.N. Bohdanovych, V.M. Bielov, P.V. Sysoiev Temperature on local sites of sliding contact, *Friction and Wear* 5 (1993) 843-880 (in Russian).
- [9] Ye.S. Socolan, The analysis of the temperature of the methods for temperature calculation under Solids friction, *Problems of Tribology* 2 (1998) 46-51 (in Russian).
- [10] Yu.G. Gogotsi, A.M. Kovalchenko, I.A. Kossko V.P. Yaroshenko, Friction interaction of ceramics on the bases of nonmetallic refractory compounds with steel, *Friction and Wear* 5 (1990) 661-667 (in Russian).
- [11] Yu.D. Tretiakov Solid phase reactions - Moscow, Khimia Published House, 1978.
- [12] G. Henrici-Olive, S. Olive The chemistry of the catalyzed hydrogenation of carbon monoxide. Moscow, Mir Published House, 1987.