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*A. Proidak, M. Hasyk, Yu. Proidak, O. Bezshkurenko***MODELING OF TEMPERATURE-CONCENTRATION RANGES OF PHASE STABILITY AND LIQUIDUS SURFACE IN THE TERNARY Fe–P–C SYSTEM AND PHASE COMPOSITION EXPERIMENTAL STUDY**

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This paper reports thermodynamic properties and phase equilibria in the iron-phosphorus-carbon system for developing a technology for smelting ferrophosphorus as well as for utilizing them in the processes of phosphorus-alloying of metals. According to the results of thermodynamic calculations, we plotted a ternary Fe–P–C phase equilibrium diagram (liquidus surface) in the form of graphical dependences, which indicate the concentration fields of phase coexistence. The results of simulation allowed finding out five nonvariant points, three of which are new:  $E_1$  eutectic ( $t_{\text{eutectic}}=1217^\circ\text{C}$ ),  $U_1$  peritectic ( $t_{\text{peritectic}}=1095^\circ\text{C}$ ), and  $E_3$  eutectic ( $t_{\text{eutectic}}=338^\circ\text{C}$ ). The experimental studies of the phase composition of ferrophosphorus showed that the phosphorus microstructure is represented by  $\text{Fe}_3\text{P}$  phosphide,  $\text{Fe}_3\text{C}$  carbide, and carbophosphide eutectic. We carried out the thermodynamic calculation of the temperature-concentration ranges of phase stability in the Fe–P–C system that are at equilibrium with the smelts of both the carbon solid solutions and phosphorus ones in  $\alpha$ - and  $\gamma$ -iron, FeP,  $\text{Fe}_2\text{P}$ ,  $\text{Fe}_3\text{P}$  phosphides, and graphite. In this study, three previously unknown nonvariant equilibria have been determined: a eutectic equilibrium at  $1216.58^\circ\text{C}$ ; a peritectic one with a transformation point at  $1095.19^\circ\text{C}$ ; and a eutectic one at a temperature of  $337.51^\circ\text{C}$ . In experiments, we obtained an equilibrium concentration of carbon which decreases in the Fe–P–C system when the content of phosphorus increases. The research findings largely reveal special features of preparation of ferrophosphorus by carbon reduction of phosphorites.

**Keywords:** ferrophosphorus, thermodynamic analysis, phosphide, carbide, carbophosphide eutectic, phase composition, phosphorite.

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**Introduction**

To improve techniques for processing complex minerals and achieve a new technological level thereof, it is important to study the properties of real heterogeneous systems. In order to conduct physicochemical analysis, state diagrams representing dependences between the composition and properties of the system are constructed. The most commonly used state diagrams show dependences between the initial composition of systems and the temperature of phase transformations occurring therein. Furthermore, physicochemical analysis determines the presence of polymorphic transformations of the system components in various aggregate states, the composition, and properties of chemical compounds formed by the

system components. The analysis also determines the temperature of all phase transformations in the systems of a given composition, as well as the changes in the composition and relative amount of phase equilibria when temperature changes. Finally, it helps to choose a composition of the most low-melting system or the most refractory one and having other valuable properties [1].

**Theory**

There are several semi-empirical methods for constructing temperature-concentration phase diagrams based on approximate free energy functions and consistent with the existing thermodynamic data. These methods can be quite useful, for example, for extrapolating phase equilibria to unknown regions of

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*Modeling of temperature-concentration ranges of phase stability and liquidus surface in the ternary Fe–P–C system and phase composition experimental study*

phase diagram space, or for calculating thermodynamic functions from strictly empirical phase equilibrium data [2,3].

Thermodynamic analysis of complex metallurgical systems that studies several phase equilibria at given temperature and pressure is a task difficult to perform. In case when there occur one or two reactions, the combination of the mass action law with the condition of the mole balance (or mass balance) of the elements enables calculating equilibrium concentrations of components [4]. For a system, where there may be multiple thermodynamically-stable compounds, numerical calculations should be performed by way of the total (stockpile) Gibbs energy minimization for the given point of composition, temperature, and pressure. This problem can be solved using corresponding algorithms and computation. As general, the basic starting equation for such calculations is the following function of the heat capacity of a phase or a compound:

$$C_p = A + B \cdot 10^{-3}T + D \cdot 10^{-6}T^2$$

where A, B, C, D are some numeric coefficients of the equation; and T is the absolute temperature, K.

Such equations are correct for a given solid phase determined by the temperature and pressure ranges where there are no polymorphic or other phase transitions. For liquid phases, it is assumed that  $c_p = \text{const}$ , since the usual comprehensive experimental data cannot accurately reveal any heat capacity dependence on the temperature.

Using common thermodynamic relations, a standard enthalpy of phase may be written in the form [4,5]:

$$H^0(T) = H_f^0(298) + \int_{298}^{T_{tr,1}} c_p(T) dT + \sum_{i=1}^n \left( H_{tr,i} + \int_{T_{tr,i}}^{T_{tr,i+1}} c_p(T) dT \right)$$

where the first member of the relation is a standard enthalpy of phase formation at 298 K, and the second one indicates the change of the enthalpy of phase in a standard condition at the temperature increase from 298 K to the temperature of the first phase transition  $T_{tr,1}$ . The third member of the relation indicates the change of the enthalpy of phase under all phase transitions that occur at the temperatures  $T_{tr,i}$ , including melting.

Likewise, the entropy is given by the following expression:

$$S^0(T) = H_f^0(298) + \int_{298}^{T_{tr,1}} \frac{c_p(T)}{T} dT + \sum_{i=1}^n \left( \frac{H_{tr,i}}{T_{tr,i}} + \int_{T_{tr,i}}^{T_{tr,i+1}} \frac{c_p(T)}{T} dT \right)$$

and Gibbs energy is expressed as follows:

$$G^0(T) = H^0(T) - T \cdot S^0(T).$$

The Gibbs energy of each phase (in the general case it is a chemical potential of a phase  $m_i$ ) is summarized with the additional contribution

$\sum_{i=1}^n RT(N_i \ln N_i)$  from the entropy of mixing  $R(N_i \ln N_i)$ , if the phase is an n-component solution with the mole fraction  $N_i$  of each component and the excess Gibbs energy  $G_m^E$  that takes into account the nonideality of the solution components of the analyzed phase ( $\Delta G_i^{\text{excess}}$ ,  $\Delta S_i^{\text{excess}}$ ,  $\Delta H_i^{\text{excess}}$ ):

$$G_m = \sum_{i=1}^n N_i \mu_i^0 + RT \sum_{i=1}^n N_i \ln N_i + G_m^E.$$

The excess Gibbs energy may be expressed by the polynomial that includes energy parameters of interaction of the solution components of various order [4]:

$$G_m^E = \sum_{i=1}^n \sum_{j=1}^n N_i N_j (L_{ij}^0 + (N_i - N_j)^2 L_{ij}^2) + \sum_{i=2}^{n-1} \sum_{j=i+1}^n N_i N_i N_j (L_{1ij} + N_i L_{11ij} + N_j L_{1ij}).$$

The foregoing form of expression is the most commonly used one (there are other models used to express the excess Gibbs energy, but in the present paper they have not been considered).

#### *Models for phase equilibria description*

The expression for  $G_m^E$  may also include additional parameters of the higher order  $L_{ijkl}$  if they are known. It should be noted, that the superscript (0, 1, 2) of the  $L_{ij}$  parameters indicates the order of interaction (zero, first, or second), but not the index of power. This model, also known as the Redlich-Kister model, is used to describe condensed phases and phase equilibria when calculating phase equilibria diagrams. The peculiarity of the method is that any of the components may be selected as a solvent. This fact is highly important when analyzing metallurgical solutions, where the changes in the phase composition occur in the wide ranges of the concentration of components.

The Gibbs energy minimization reduces to searching for such  $N_i$  combination (i.e. the solution composition) at a given temperature, pressure, and balance of masses (number of moles) at which Gibbs energy magnitude is minimal. The obtained calculations are graphically represented as the phase equilibria diagrams (in the function of composition, temperature, and/or pressure).

The Butler equation [6–9] is applicable to the model of the equilibrium grain boundary energy and the equilibrium composition of boundaries in polycrystals depending on the bulk composition, temperature, pressure, and five degrees of freedom. In the simplest case of an optimal solution and equal atomic sizes of the components, the Butler equation reduces to the well-known McLean equation [10].

**The thermodynamic modeling technique for the phase equilibria and liquidus surface in the Fe–C–P ternary system**

Earlier [5], the phase equilibria modeling was performed with the use of THERMOCALC Version R software package. Figure 1 shows the basic modules of the software package used in the calculations as well as the correlation thereof.

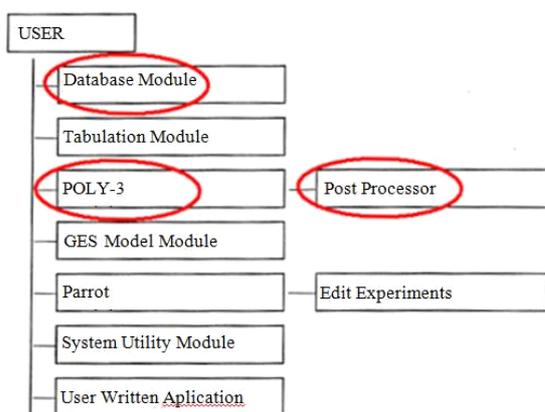


Fig. 1. Modules of THERMOCALC program

Database module is used in the beginning to select the corresponding databases and optimal parameters for the analyzed solutions. POLY-3 Module includes thermodynamic data in the tabulated form needed for the equilibrium calculations. Post Processor provides

the output of the modeling results in the graphic form (images of phase equilibrium diagrams).

**Iron phosphides**

In the Fe–P binary system [11,12], there are three phosphides with the chemical composition and enthalpy of formation values given in Table 1 [13].

The peritectic transformation of  $\text{Fe}_3\text{P}$  phosphide occurs at 1166°C, while the congruent melting of  $\text{Fe}_2\text{P}$  takes place at 1370°C. However, the data on FeP melting point are unreliable.

In this system, on the side of the iron angle of the diagram there is the eutectic (E) with coordinates 16.9 at.% P (10.2 wt.% P) and the temperature of 1048°C. The eutectic in the  $\text{Fe}_2\text{P}$ –FeP system exists at 40 at.% (27 wt.%) of phosphorus at the temperature of 1262°C. Phosphorus as a ferrite promoter narrows g-area that has a maximum phosphorus concentration of 0.3 at.% (0.2 wt.%).

**Modeling of Fe–P–C system**

The thermodynamic modeling [5] was conducted using the THERMOCALC software integrated with the ThermoCalc R-SSOL2 database. The phase equilibrium diagram of the ternary Fe–P–C composition (liquidus surface) obtained as a result of modeling is given in Fig. 2.

The main assumption accepted when implementing the model was that only stable phases had been taken into account (particularly, carbon in the form of graphite), while a metastable phase, cementite, was not been considered. The specific character of the calculation results obtained from THERMOCALC is that in Fig. 3 the weight percent of carbon (from 0 to 0.05, i.e. up to 5%) and phosphorus (from 0 to 0.20, i.e. up to 20%) in the liquid phase are plotted on the composition axes. The black thin lines are isothermal curves in increments of 100°C, the numbers on them show the temperature value calculated by  $t=400+300n$  (for instance, number «3» stands for the isothermal curves  $400+300\cdot3=1300^\circ\text{C}$ , and number «2» implies  $400+300\cdot2=1000^\circ\text{C}$ ). In Fig 3 (on the right), the red lines separate phase boundaries.

The temperature is represented by the isothermal curves (black lines) in increments of 100°C; the numbers on them show the temperature value that is determined by  $t=700+60n$  (for example, number «5»

Table 1

**Chemical composition and enthalpy of formation of compounds in the Fe–P binary system**

Composition	Phosphorous/carbon content, wt.%	Enthalpy of formation, $-\Delta H_{298}^0$ , kJ/mol
$\text{Fe}_3\text{P}$	15.57	163.0
$\text{Fe}_2\text{P}$	21.83	158.8
FeP	37.34	121.2
$\text{Fe}_3\text{C}$	6.67	24.9

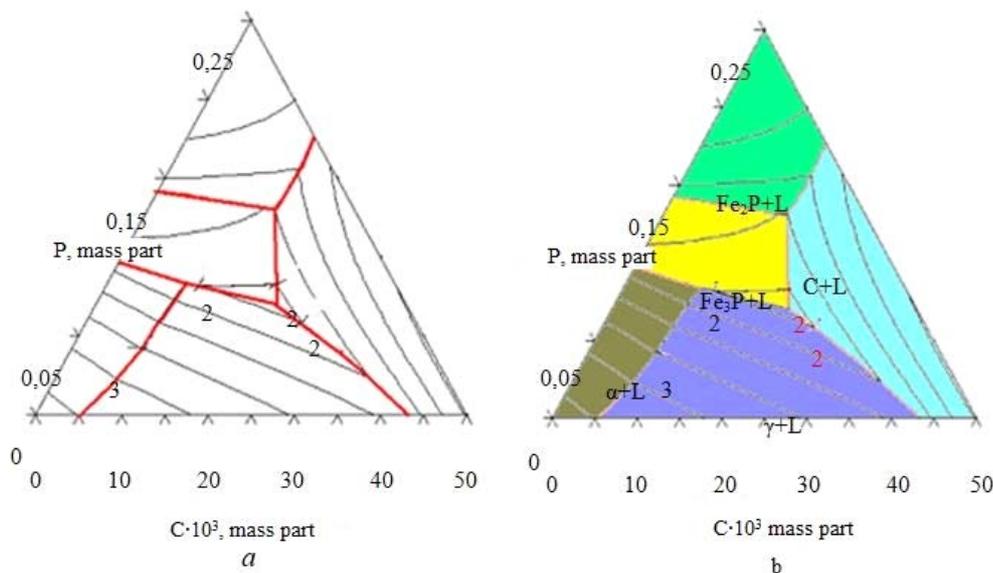


Fig. 2. Liquidus surface of the Fe–P–C system: a – concentration fields of the phase coexistence; b – the same diagram where phase diagram sections are colored

stands for the temperature «mark»  $700+60.5=1000^{\circ}\text{C}$ ). The red lines separate at least one phase change at the imaging point movement; the phase fields of the stable phases are colored (as in Fig. 2).

A similar liquidus surface, but on the Cartesian axes, is presented in Fig. 3.

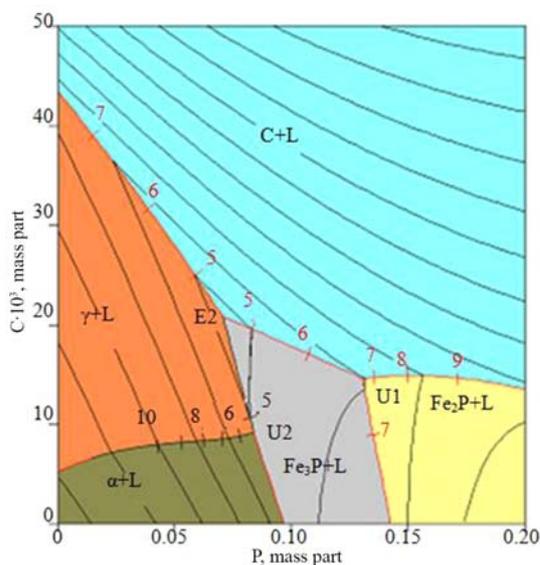


Fig. 3. Phase equilibria in the Fe–P–C system (the Cartesian coordinate system referred to in the text)

The nonvariant equilibria are represented by the eutectic points (E) and peritectic points (U). Three out of five possible points in the Fe–P–C system,  $U_1$ ,  $U_2$ , and  $E_2$ , fall within the diagram field in Fig. 4.

The temperatures and nonvariant equilibria reactions are given in Table 2.

Table 2

**Temperatures and nonvariant equilibria reactions**

Nonvariant equilibria	Temperature, $^{\circ}\text{C}$	Equilibrium reaction
$E_1$	1216.58	$L=\text{Fe}_2\text{P}+\text{FeP}+\text{C}_{\text{graphite}}$
$U_1$	1095.19	$L+\text{Fe}_2\text{P}=\text{Fe}_3\text{P}+\text{C}_{\text{graphite}}$
$U_2$	1005.55	$L+\alpha\text{-Fe}=\gamma\text{-Fe}+\text{Fe}_3\text{P}$
$E_2$	959.62	$L=\gamma\text{-Fe}+\text{Fe}_3\text{P}+\text{C}_{\text{graphite}}$
$E_3$	337.51	$L=\text{FeP}+\text{C}_{\text{graphite}}+\text{P}_{\text{crystal}}$

Moreover, as a result of the modeling of Fe–P–C system, there have been discovered five nonvariant points, and only two of them were previously known [14]:

the eutectic  $E_2$ , that corresponds to the reaction  $L=\gamma\text{-Fe}+\text{Fe}_3\text{P}+\text{C}_{\text{graphite}}$  ( $t=958^{\circ}\text{C}$ ); the peritectic  $U_2$ , corresponding to the reaction  $L+\alpha\text{-Fe}=\gamma\text{-Fe}+\text{Fe}_3\text{P}$  ( $t=1006^{\circ}\text{C}$ ).

Another three nonvariant points  $E_1$ ,  $U_1$ , and  $E_3$  have been discovered in the present study for the first time.

**Modeling of phosphorus influence on carbon solubility in Fe–P–C-based model alloys and determination of the coexistence curves and nonvariant points of the equilibrium phases coexistence**

Schurmann et al. [14,15] experimentally studied influence of phosphorus on carbon solubility in the model alloys in the Fe–P–C stable system and determined the coexistence curves. Due to the limited

availability of the foregoing original papers, the analysis of Fig. 5 representing the liquidus surface projection of the Fe–P–C stable system is given below.

In particular, it is interesting to note that in the given diagram [8] there are several nonvariant points and letters ( $\alpha$ ,  $\gamma$ ) designating ferrite and austenite respectively.

It follows from the works [14,15] that the point B plotted on the axis representing the carbon content is a nonvariant point in the Fe–C system that corresponds to the peritectic equilibrium  $L_b + \delta \leftrightarrow \gamma$  at 1493°C (the liquid phase  $L_b$  contains 0.533% of C).

The point C on the vertical axis showing the carbon content is also a nonvariant one and corresponds to the eutectic equilibrium  $L_c \leftrightarrow \gamma + C$  at 1153°C (the liquid phase  $L_c$  contains 4.3% of C). Further, in the Fe–P system, the nonvariant eutectic point E refers to the eutectic equilibrium  $L_1 \leftrightarrow \alpha + Fe_3P$  at 1039°C; the liquid phase contains 10.5 at.% of P. Next, the nonvariant point U corresponds to the peritectic equilibrium  $L_u + \alpha \leftrightarrow Fe_3P$  at 1004°C (the liquid phase  $L_u$  contains 0.80 at.% of C and 8.55 at.% of P). Finally, the nonvariant point  $L_2$  represents the eutectic equilibrium  $L_2 \leftrightarrow \gamma + C + Fe_3P$  at 977°C (the liquid phase  $L_2$  contains 1.7% of C and 7.6% of P).

*Comparison of the results of the analysis of the phase equilibria and the microstructure of ferrophosphorus samples*

The phase equilibria analysis in the ternary Fe–P–C system with the phosphorus content up to 16 wt.% indicates that ferrophosphorus of the engineering grades has a complex phase composition, including phosphides, iron carbides, and carbophosphide eutectic. Figures 4–5 show microstructures of the two areas of a sample, captured at 1800 and 2500 magnification, as well as the spectral recordings that indicate the presence of the particular chemical elements in the corresponding structures.

When examining a microstructure, one can distinguish three phases of different colors and morphology: a grey phase, a dark one, and a eutectic. The results of X-ray spectral microanalysis of a ferrophosphorus microstructure conducted in the mapping mode (Figs. 6 and 7) suggest that phosphorus is concentrated in the grey phase, while the concentration of carbon is found in the dark one.

It is interesting to note that the data of the spectral recordings B in Figs. 4 and 5 prove the presence of various quantities of Fe, P, C and Si in the phase structures. The analyzed areas of the constituents have been marked with the frames. The chemical composition of these microregions obtained as a result of X-ray spectral microanalysis are given in tables of Figs. 4 and 5.

The data provided in the tables alongside the

results of the microstructure analysis prove that the grey phase is represented by  $Fe_3P$  phosphide (the frames 001, 005, and 008), the dark phase is iron carbide (the frames 003, and 007), and the «striped» structure is carbon phosphide eutectic (the frames 002, 004, and 006).

It is seen that the ferrophosphorus structure formation occurred from the smelt with 12.6% of P and 1.4% of C, so that the alloy basis of the analyzed sample is represented by  $Fe_3P$  phosphide. It should be noted, that the white lines that mainly border eutectic formations create shadows due to the relief of the etched structure. A small amount of silicon is concentrated in the content of eutectic formations (the frames 002, 004, and 006) [16].

### Conclusions

In this paper, the significance of the research of the thermodynamic characteristics and phase equilibria in the Fe–P–C system has been grounded in terms of the ferrophosphorus smelting technique development.

The thermodynamic modeling of the temperature-concentration ranges of phase stability in the Fe–P–C system that are at equilibrium with the smelt of both the carbon solid solutions and phosphorus ones in  $\alpha$ - and  $\gamma$ -iron, FeP,  $Fe_2P$ ,  $Fe_3P$  phosphides, and graphite has been carried out with the use of THERMOCALC programs package integrated with the ThermoCalc R–SSOL2 database. Furthermore, the liquidus surface of the ternary iron-phosphorus-carbon system has been constructed. As a result of the Fe–C–P system thermodynamic modeling, three previously unknown nonvariant equilibria have been found out: the eutectic  $L = Fe_2P + FeP + C_{\text{graphite}}$  that occurs at the temperature of 1216.58°C; the peritectic  $L + Fe_2P = Fe_3P + C_{\text{graphite}}$  with the transition temperature of 1095.19°C; and the eutectic  $L = FeP + C_{\text{graphite}} + P_{\text{crystal}}$  at the temperature of 337.51°C. The existence of  $L = \gamma\text{-Fe} + Fe_3P + C_{\text{graphite}}$  in the eutectic system and  $L + \alpha\text{-Fe} = \gamma\text{-Fe} + Fe_3P$  in the peritectic system has been proved and the equilibria temperatures thereof have been specified as follows:  $t_{\text{eutectic}} = 959.62^\circ\text{C}$ ; and  $t_{\text{peritectic}} = 1005.55^\circ\text{C}$ .

Analysis of publications on the binary Fe–P system and the ternary Fe–P–C system reveals that ferrophosphorus of the engineering grades must have complex phase composition that alters when the phosphorous content increases. With the phosphorus content increase, the decreasing of the equilibrium carbon concentration in the Fe–P–C system is observed due to the higher thermodynamic strength of the chemical bond of elements in the Fe–P system in contrast to the Fe–C system, compare:  $\Delta H_{298}^0 (Fe_3P) = -213.53 \text{ kJ/mol}$  and

$$\Delta H_{298}^0 (Fe_3C) = -24.9 \text{ kJ/mol.}$$

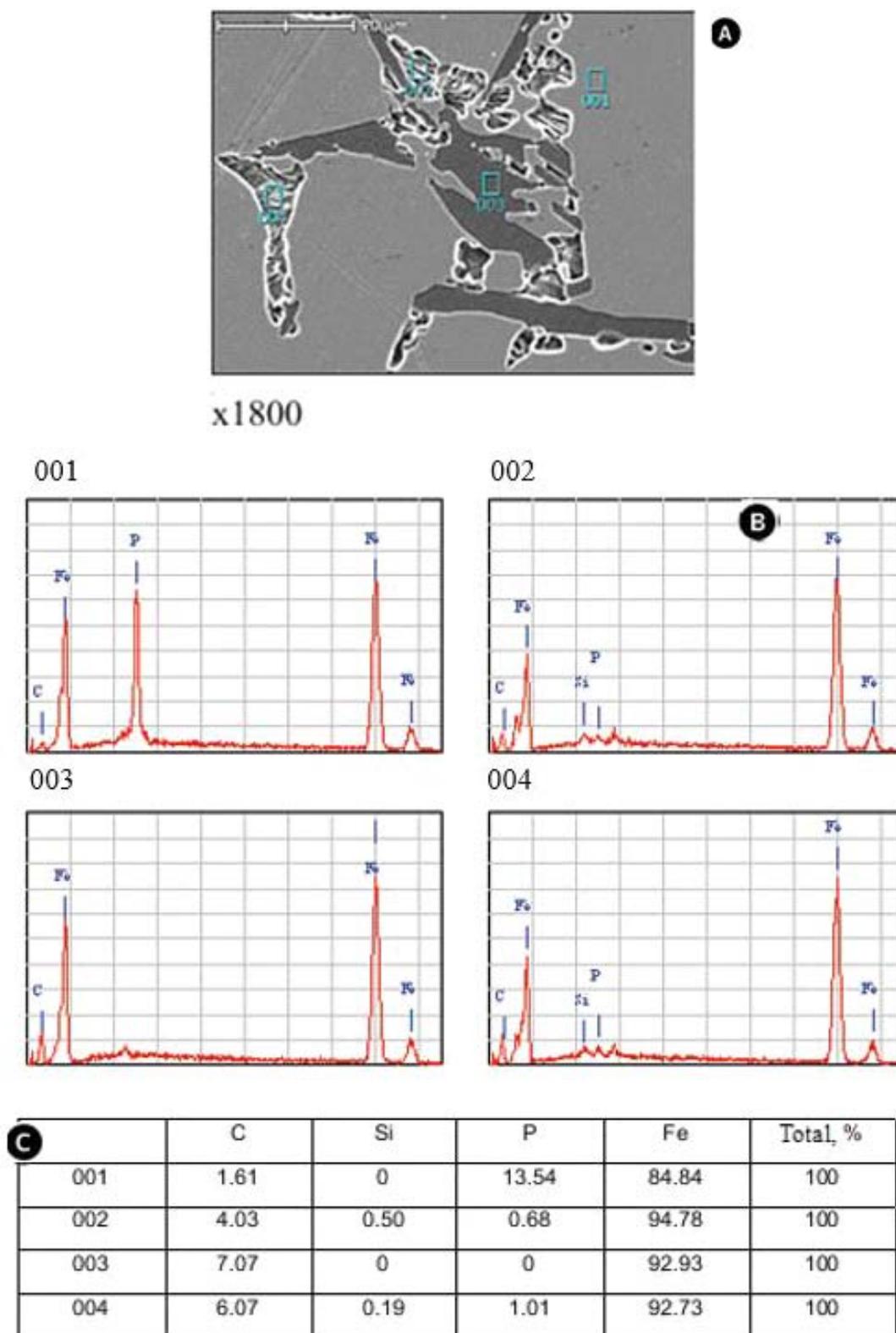


Fig. 4. Results of X-ray spectral microanalysis of the chemical phase composition in ferrophosphorus microstructure r1800:

A – the analyzed areas, marked with the frames; B – spectrograms of the analyzed areas; and C – the approximate chemical composition based on X-ray spectral microanalysis

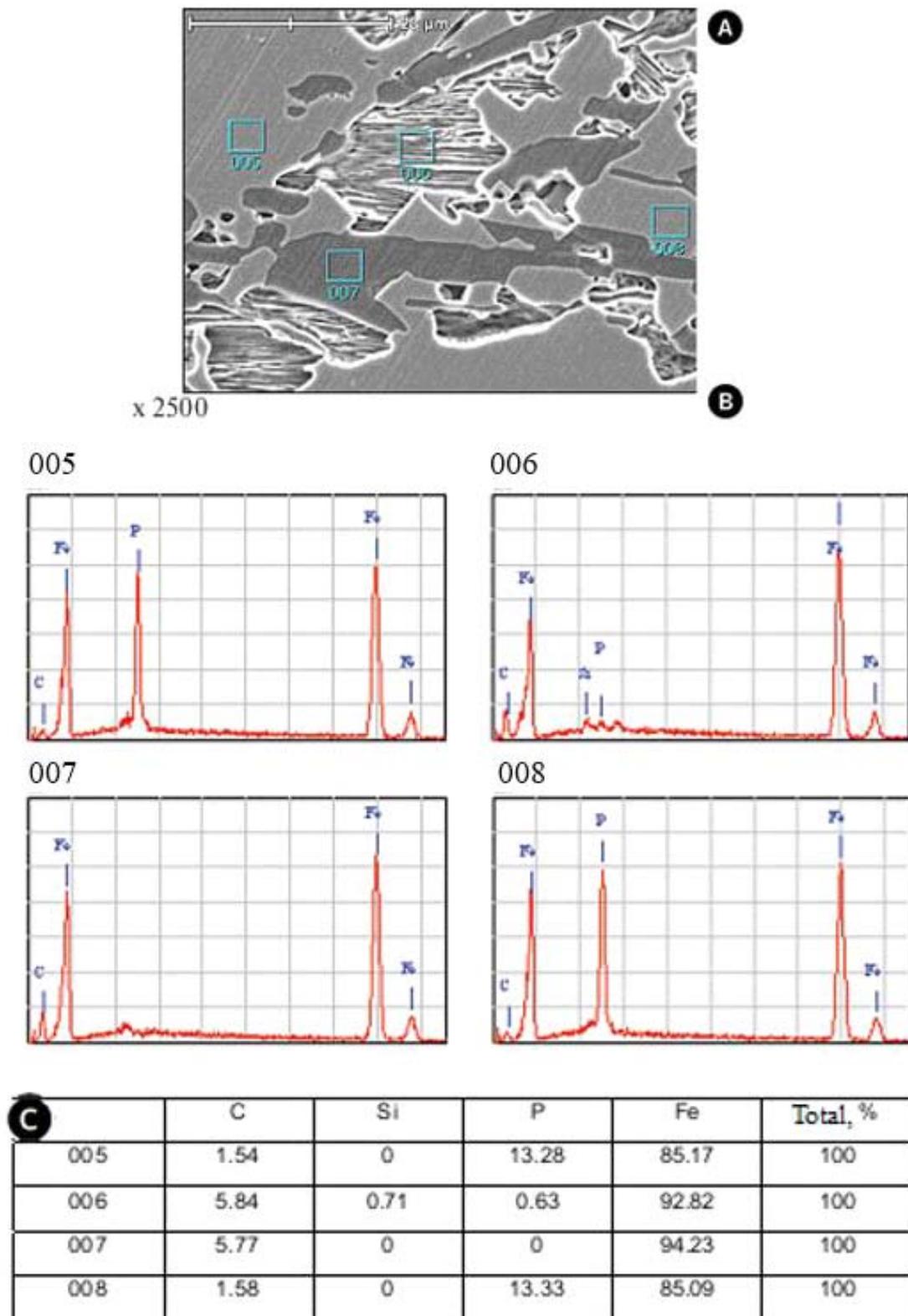


Fig. 5. Results of X-ray spectral microanalysis of the chemical phase composition in the microstructure of the ferrophosphorus sample: A – the analyzed areas are marked with the frames; B – spectrograms of the analyzed areas; and C – the approximate chemical composition based on the X-ray spectral microanalysis results

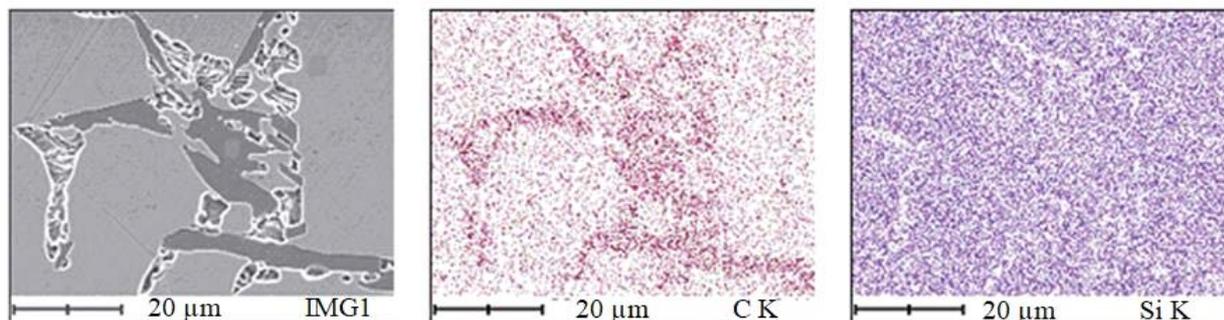


Fig. 6. Results of X-ray spectral microanalysis of the ferrophosphorus microstructure in the mapping mode (the brighter color indicates the higher content of the element)

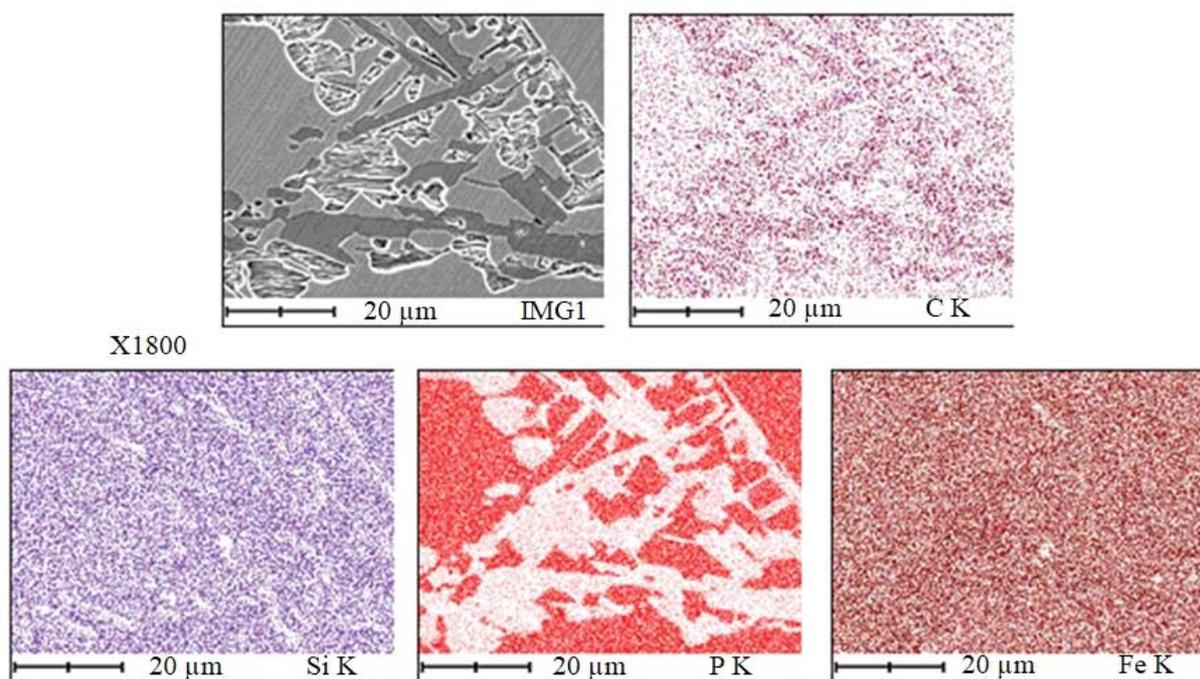


Fig. 7. Results of X-ray spectral microanalysis of the ferrophosphorus microstructure carried out in the mapping mode (the brighter color indicates the higher content of the element)

The precise electron microscope investigation of the phase composition of ferrophosphorus obtained by the carbon reduction smelting of the domestic phosphorite in the graphite crucible in the resistance furnace has been conducted. It has been discovered that the ferrophosphorus microstructure is represented by  $\text{Fe}_3\text{P}$  phosphide,  $\text{Fe}_3\text{C}$  carbide and carbon phosphide eutectic. The reported results were used when conducting experimental smelting in the induction furnace graphite crucible, aimed to obtain ferrophosphorus by carbon reduction of the phosphorites from the Malokamyshevskiy deposit.

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#### МОДЕЛЮВАННЯ ТЕМПЕРАТУРНО-КОНЦЕНТРАЦІЙНИХ ІНТЕРВАЛІВ ФАЗОВОЇ СТАБІЛЬНОСТІ І ПОВЕРХНІ ЛІКВІДУСУ В ПОТРІЙНІЙ СИСТЕМІ Fe–P–C І ДОСЛІДЖЕННЯ ФАЗОВОГО СКЛАДУ

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У роботі досліджено термодинамічні властивості та фазові рівноваги в системі залізо-фосфор-вуглець для розробки технології виплавки ферофосфору, а також для їх використання в процесах фосфорного легування металів. За результатами термодинамічних розрахунків розраховано діаграму потрійної фазової рівноваги Fe–P–C (поверхня ліквідусу) у вигляді графічних залежностей, що вказують концентраційні поля співіснування фаз. Результати моделювання дозволили виявити п'ять неваріантних точок, три з яких є новими: евтектика  $E_1$  ( $t_{\text{евтектика}}=1217^\circ\text{C}$ ), перитектика  $U_1$  ( $t_{\text{перитектика}}=1095^\circ\text{C}$ ) і евтектика  $E_3$  ( $t_{\text{евтектика}}=338^\circ\text{C}$ ). Експериментальні дослідження фазового складу ферофосфору показали, що мікроструктура фосфору надана фосфідом  $\text{Fe}_3\text{P}$ , карбідом  $\text{Fe}_3\text{C}$  і евтектикою карбофосфіду. Термодинамічне моделювання температурно-концентраційних діапазонів фазової стабільності проведено для системи Fe–P–C, в якій знаходяться в рівновазі з розплавами як вуглецеві тверді розчини, так і фосфорні в  $\alpha$ - і  $\gamma$ -залізі, фосфідах  $\text{FeP}$ ,  $\text{Fe}_2\text{P}$ ,  $\text{Fe}_3\text{P}$  та графіті. У цьому дослідженні було визначено три раніше невідомі неваріантні рівноваги: евтектична рівновага при  $1216,58^\circ\text{C}$ ; перитектичний з температурою перетворення  $1095,19^\circ\text{C}$ ; і евтектичний при температурі  $337,51^\circ\text{C}$ . У експериментах було одержано рівноважну концентрацію вуглецю, яка зменшується в системі Fe–P–C зі збільшенням вмісту фосфору. Результати досліджень значною мірою розкривають особливості одержання ферофосфору вуглецевим відновленням фосфоритів.

**Ключові слова:** ферофосфор, термодинамічний аналіз, фосфід, карбід, карбофосфідна евтектика, фазовий склад, фосфорид.

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**MODELING OF TEMPERATURE-CONCENTRATION RANGES OF PHASE STABILITY AND LIQUIDUS SURFACE IN THE TERNARY Fe–P–C SYSTEM AND PHASE COMPOSITION EXPERIMENTAL STUDY**

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This paper reports thermodynamic properties and phase equilibria in the iron-phosphorus-carbon system for developing a technology for smelting ferrophosphorus as well as for utilizing them in the processes of phosphorus-alloying of metals. According to the results of thermodynamic calculations, we plotted a ternary Fe–P–C phase equilibrium diagram (liquidus surface) in the form of graphical dependences, which indicate the concentration fields of phase coexistence. The results of simulation allowed finding out five nonvariant points, three of which are new: E<sub>1</sub> eutectic (t<sub>eutectic</sub>=1217°C), U<sub>1</sub> peritectic (t<sub>peritectic</sub>=1095°C), and E<sub>3</sub> eutectic (t<sub>eutectic</sub>=338°C). The experimental studies of the phase composition of ferrophosphorus showed that the phosphorus microstructure is represented by Fe<sub>3</sub>P phosphide, Fe<sub>3</sub>C carbide, and carbophosphide eutectic. We carried out the thermodynamic calculation of the temperature-concentration ranges of phase stability in the Fe–P–C system that are at equilibrium with the smelts of both the carbon solid solutions and phosphorus ones in α- and γ-iron, FeP, Fe<sub>2</sub>P, Fe<sub>3</sub>P phosphides, and graphite. In this study, three previously unknown nonvariant equilibria have been determined: a eutectic equilibrium at 1216.58°C; a peritectic one with a transformation point at 1095.19°C; and a eutectic one at a temperature of 337.51°C. In experiments, we obtained an equilibrium concentration of carbon which decreases in the Fe–P–C system when the content of phosphorus increases. The research findings largely reveal special features of preparation of ferrophosphorus by carbon reduction of phosphorites.

**Keywords:** ferrophosphorus; thermodynamic analysis; phosphide; carbide; carbophosphide eutectic; phase composition; phosphorite.

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