Study of the Chemical Interactions Between Iron Phosphides and Iron Silicides

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Abstract

This article contains the research results of the thermodynamic modeling of interaction of iron phosphides Fe_2P and FeP with $FeSi_2$, obtained by a method of the total thermodynamic analysis on the basis of the program HSC-5.1 of the Finnish metallurgical company Outokumpu, developed on both a principle of the Gibbs energy minimization, and also kinetics of the phosphorus release by ferrosilicon from the electrothermal ferrophosphorus − a by-product of the yellow phosphorus production.

It was found, that temperature of the beginning of the phosphorus formation in systems iron phosphides − $FeSi_2$ depends on a mole ratio of phosphorus in the phosphides. At the increasing this ratio from 33.3 to 50%, the temperature of the beginning of the phosphorus formation decreases from 1362 K to 1290 K. At lower temperature (773 K) there is the formation of intermediate FeP_2 and FeP in a system Fe_2P-$FeSi_2$ and intermediate FeP_2 in a system FeP-$FeSi_2$, which react with $FeSi_2$ with temperature increasing and form a gaseous phosphorus. The process proceeds in kinetic mode and is characterized by apparent activation energy of 281-389 kJ/mol.

Introduction

As mentioned by Ershov − in theelectrothermal production of yellow phosphorus from raw materials of phosphorite, quartzite and coke, 1000 kg of phosphorus rise up to 300 kg of ferrophosphorus [1]. The main consumer of ferrophosphorus is the ferrous metallurgy, in which ferrophosphorus is used for smelting of alloyed phosphorus-containing steels (for example automatic steels), iron casting. However, recently in spite of the introduction of technical requirements [2] in industrial enterprises, considering chemical heterogeneity of ferrophosphorus concerning P, Mn, Si and the presence of slag inclusions a firm demand on the electrothermal ferrophosphorus [3] has decreased, and in connection with this fact a need of a search of a rational method of the electrothermal ferrophosphorus processing has arisen.

The world practice suggests some directions of the ferrophosphorus processing [3-13] with the pro-duction of different products: I) phosphate slags; II) iron phosphates; III) phosphorus silicates; IV) phosphates of alkaline metals; V) a powder for corrosion-resistant coatings; VI) phosphorus (III) oxide; VII) phosphorus (V) oxide; VIII) elemental phosphorus; IX) phosphoric acid; X) phosphorus chloride; XI) phosphorus sulphide; XII) aluminium and iron phosphides. However the known methods of the ferrophosphorus processing have essentially technological and economic disadvantages.

Within the aim of search of a rational way of the ferrophosphorus processing, we took as a principle the ability of silicon to displace phosphorus from an iron phosphide melt. However, unlike the known ways of the phosphorus production from ferrophosphorus according to the reactions (Eq.1 and Eq.2), we have chosen silicon silicides as a siliceous component instead of an expensive silicon or a mixture of SiO_2 and C. As shown in Eq.1 and Eq.2 in a former work we have investigated the reaction between Fe_2P and $FeSi_2$ [14]:

$$Fe_2P + 2Si = 2FeSi + 0.5P_2 \qquad (Eq.1)$$

$$Fe_2P + 2SiO_2 + 4C = 2FeSi + 0.5P_2 + 4CO \qquad (Eq.2)$$

$$Fe_2P + 2FeSi_2 = 4FeSi + 0.5P_2 \qquad (Eq.3)$$
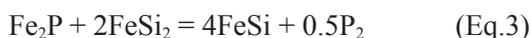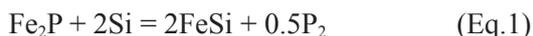
which appears more preferable than the reaction between Fe_2P, SiO_2 and C given in Eq.2.

It was found that the reaction (Eq.3) begins at 783 K, while the Eq.2 reaction starts only at 1573 K. Besides, the reaction (Eq.3) is characterized by the power inputs 648 kW·hour/t of phosphorus, and for the reaction (Eq.2) an input of 4600 kW·hour/t is necessary.

Industrial ferrophosphorus contains 12-27 mass % of phosphorus. Depending on a phosphorus content, ferrophosphorus consists of various amounts of Fe_3P, Fe_2P, FeP, FeP_2 [1, 15]. This article contains the research results of the thermodynamic modeling of interaction of Fe_2P and FeP with $FeSi_2$, and also the research results of kinetics of the phosphorus release from ferrophosphorus produced by the Open Company "Kazphosphate" at the presence of ferrosilicon of grade FS 65.

Research approach

The thermodynamic research of the interaction of iron phosphides with $FeSi_2$ was carried out using the program HSC-5.1 (Outokumpu), based on the principle of the Gibbs energy minimization [16, 17]. The subprogram "Reaction Equations" was used for the calculation of ΔG_t^0 and ΔH_t^0, and the subprogram "Equilibrium Compositions" – for the calculation of an equilibrium degree of elements' distribution in the investigated systems.

The experimental investigation of the kinetics of phosphorus release at the chemical interaction of ferrophosphorus and ferrosilicon was carried out in the St. Petersburg Technological University using an induction heating unit. An initial charge (100-110 g) was placed in a graphite crucible which was put into a furnace and kept in due time for melting in the furnace. The furnace temperature was measured by an optical pyrometer and a tungsten-rhenium thermocouple. After the experiment was terminated the crucible was taken out of the furnace. The cooled melt was weighed and analyzed for phosphorus content by the technique described in [2]. Some samples were analyzed by a scanning electron microscope JSM-6490LM (JEOL, Japan) and also by an X-ray diffractometer D8 Advance (Bruker). A degree of the phosphorus release in a gas phase (α_P, %) was determined according to the results of chemical analyses of the ferrophosphorus and the melt formed

on phosphorus content using the following equation:

$$\alpha_P \frac{G_{FP} \cdot C_{P(FP)} - G_{melt} \cdot C_{P(melt)}}{G_{FP} \cdot C_{P(FP)}} \cdot 100 \qquad (Eq.4)$$

where G_{FP} and G_{melt} – masses of the used ferrophosphorus and the produced melt accordingly (g);

$C_{P(FP)}$ and $C_{P(melt)}$ – phosphorus content in the initial ferrophosphorus and in the melt accordingly (parts of unity).

At the experiment carrying out we used the electrothermal ferrophosphorus of a grade FeP 20-6 of the Open Company "Kazphosphate" and the ferrosilicon of a grade FS 65 [19] (Table 1).

Table 1
Chemical composition of the used FP and FS

Content (mass %)	P	Si	Mn	Al	Fe	other
FP	26.4	1.3	4.5	-	66.0	1.8
FS 65	-	63.8	0.6	1.1	33-1	1.4

X-ray patterns and electron microscopy of initial substances are represented in Figs. 1 and 2 respectively.
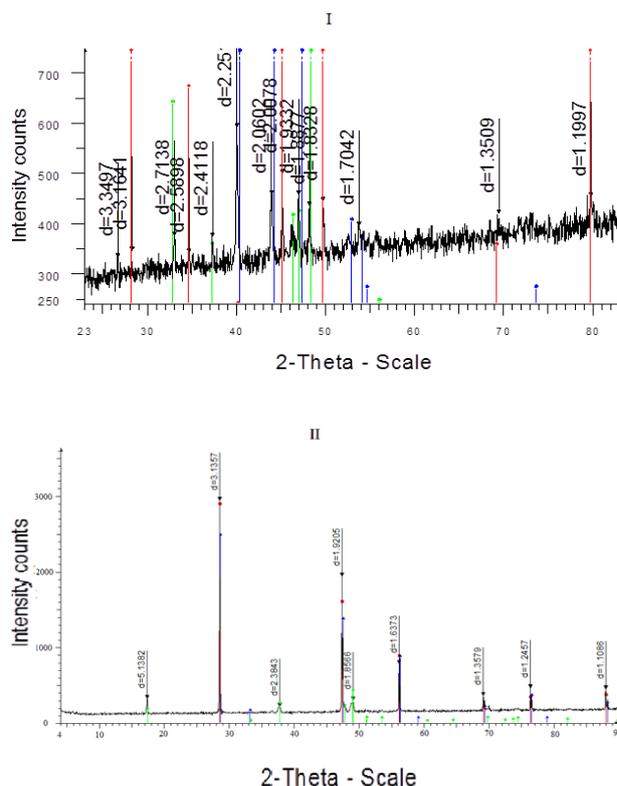
Fig. 1. X-ray diffraction patterns of the ferrophosphorus FeP 20-6 (I) and the ferrosilicon FS 65 (II).
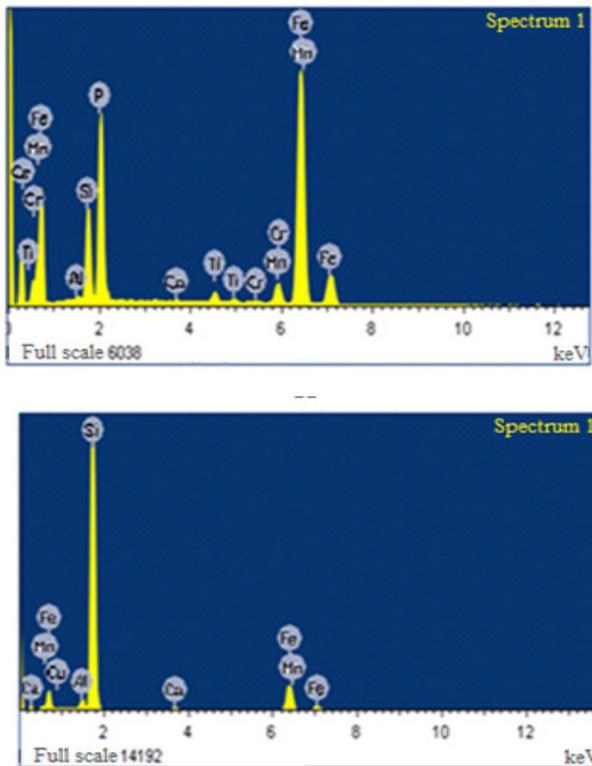
Fig. 2. Electron microscopy of the ferrophosphorus FeP 20-6 (I) and the ferrosilicon FS 65 (II).

Table 2
Chemical and phase analysis obtained
from Figs. 1 and 2

Compound Name	Formula	% mass
Iron Phosphide	FeP	44.3
M Barringerite, syn	Fe_2P	33.1
Iron Silicon	FeSi	22.6

Compound Name	Formula	% mass
Iron Phosphide	Si	26.1
Ferdisilicite, syn (NR)	FeSi	6
Iron Silicon	$FeSi_2$	67.9

For the description of the phosphorus release process from the ferrophosphorus at the presence of the ferrosilicon the equation (Eq.5) was used:

$$\alpha = 1-\exp[-k \cdot \tau^n], \qquad (Eq.5)$$

where k and n are empirical coefficients, τ – duration of the process (minutes), α – degree of realization of the process (parts of unity) [20]. A speed of the phosphorus release from the ferrophosphorus (V) according to the IUPAC recommendations [21] was determined on the basis of the formula $V = d\alpha/d\tau$. In

our case a speed of the phosphorus release from the ferrophosphorus was calculated by means of differentiation of the equation (Eq.5) [22] which gives:

$$V = \frac{d\alpha_P}{d\tau} = n \cdot k^{1/n} \cdot [-\ln(1-\alpha)^{1-\frac{1}{n}}] \cdot (1-\alpha) \qquad (Eq.6)$$

The equation (Eq.6) allows estimating the speed of the process for every value of the phosphorus extraction if the coefficients "n" and "k" are known. After transformation of the exponential equation (Eq.5) in the linear equation:

$$ln[-ln(1-\alpha)] = lnk + n \cdot ln\tau, \qquad (Eq.7)$$

empirical coefficients of the equation were determined by means of a graphic representation of the experimental results in coordinates $ln[-ln(1-\alpha)]$ – $ln\tau$. The coefficient "n" is determined as a slope of the straight line to the axis $ln\tau$, and the coefficient "k" – on the basis of the lnk value as a segment intercepted by the straight line on the ordinate axis at $ln\tau = 0$.

For the calculation of apparent activation energy of the process (E_{ap}) according to [23-25] we determined a dependence $lgV = f(^1/_T)$ for fixed values α. Then E_{ap} was estimated using Eq.8:

$$E_{ap} = 2.303 \cdot 8.314 \cdot |tg\varphi| \qquad (Eq.8)$$

where φ – inclination of the line to the abscissa axis, 8.314 – the universal gas constant (J/(mole*K)), E_{ap} – apparent activation energy (J/mole).

Results and Discussion

Thermodynamic Analysis

For the system $Fe_2P-2FeSi_2$. As can be predicted from Eq.3 the results of the thermodynamic modeling show that in the temperature range (773-2273 K), basic compounds are FeP_2, FeP, Fe_3P, P_4, P_2, FeSi, $FeSi_2$, Fe_5Si_3 (Fig. 3). The phosphorus distribution in the system at 773 K is the following: 91% in FeP_2 and 9% in FeP. Thus 46.4% of silicon passes into FeSi, and 53.6% remains in $FeSi_2$. The distribution degree of iron (α) in the system at 773 K is given in Table 3:

Table 3
Distribution coefficient α of Fe in the system at 773 K

α_{Fe} (%)	46.3	28	21.5	3.9	<0.1
Compound	FeSi	$FeSi_2$	FeP_2	FeP	Fe_2P

Table 4
Temperature effect on ΔG_T^0 of the formation reactions from Fe_2P and FeP

Reaction number	ΔG_T^0, kJ/mole of Fe_2P									
	573 K	673 K	873 K	973 K	1073 K	1173 K	1273 K	1373 K	1473 K	1573 K
Eq.9	-47.80	-48.78	-51.01	-52.43	-53.85	-55.67	-57.07	-59.68	-62.11	-64.81
Eq.10	-58.68	-59.97	-62.87	-64.35	-66.05	-67.92	-69.96	-72.18	-74.63	-77.27

Table 5
Temperature effect on ΔG_T^0 of the reaction (Eq.15)

T (K)	573	773	873	973	1073	1173	1373	1573
ΔG_T^0 (kJ/mole of FeP)	-21.74	-23.00	-23-54	-24.02	-24.41	24.71	-25.03	-24.92

The beginning (1%) of the formation of a gaseous phosphorus as P_4 and P_2 in the system is observed at 1362 K. A degree of the phosphorus transformation in the gaseous P_2, P_4 (α_{Pg}) at 1973 K is equal to 96.7% and at 2173 K is equal to 99.9%.

The formation of FeP_2 and FeP in the system Fe_2P-$3FeSi_2$ observed at low temperature, most probably, is connected within the reactions:

$$Fe_2P + FeSi_2 = FeP + 2FeSi \qquad (Eq.9)$$

$$2Fe_2P + 3FeSi_2 = FeP_2 + 6FeSi \qquad (Eq.10)$$
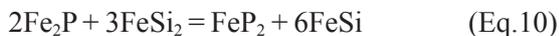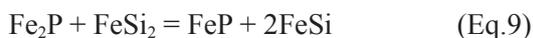
which are possible already at 573 K on the basis ΔG_T^0 calculated [16] (Table 4).

Then, with the rising temperature, the FeP_2 (Eq.10) and FeP (Eq.9) react with $FeSi_2$:

$$FeP_2 + FeSi_2 = 2FeSi + P_2 \qquad (Eq.11)$$

$$FeP + FeSi_2 = 2FeSi + 0.5P_2 \qquad (Eq.12)$$
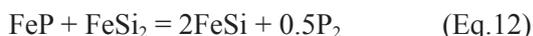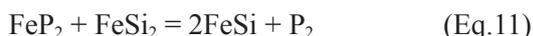
For these systems temperatures of the beginning equilibrium reaction ($\Delta G_T^0 = 0$) are 1583 K and 1393 K accordingly.

Similarly the reactions 9-12 lead to the following reactions (Eq.13 and Eq.14):

$$3Fe_2P + 6FeSi_2 = 12FeSi + 1.5P_2 \qquad (Eq.13)$$
or
$$Fe_2P + 2FeSi_2 = 4FeSi + 0.5P_2. \qquad (Eq.14)$$

Regarding the phosphorus, at the temperature increase the chemical interaction of Fe_2P with $FeSi_2$ takes place stepwise according to the scheme: $Fe_2P \rightarrow (FeP_2, FeP) \rightarrow P_2$.

Concerning the system FeP-$FeSi_2$, as can be predicted from Eq.12, the formation of FeP_2 and $FeSi$ (Fig. 3) at 773 K is a result of the following reaction (Eq.15):

$$2FeP + FeSi_2 = FeP_2 + 2FeSi \qquad (Eq.15)$$
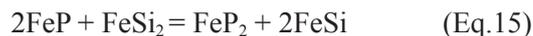
which is possible already at 573 K on the basis of the ΔG_T^0 calculation [16] (Table 5).

In the given system, in which an atomic ratio of phosphorus (0.5) in the ferrophosphorus 1% of the gaseous phosphorus formation is observed at 1290 K and notably the temperature of the beginning has been reduced by 72 K in comparison with the system Fe_2P-$FeSi_2$, in which an atomic fraction of phosphorus in the ferrophosphorus makes 33.3%. A complete termination of the phosphorus release (99.8 %) from the system FeP-$FeSi_2$ takes place at 2073 K, this temperature is 100 K less, than the respective temperature for the system Fe_2P-$FeSi_2$.

On the basis of the results of the thermodynamic calculation within the temperature range (773-2073 K), the chemical interaction in the system (concerning phosphorus) occurs according to (Eq.16):

$$FeP \rightarrow FeP_2 \rightarrow P_2 \qquad (Eq.16)$$

Kinetics Processes

The kinetics of the phosphorus extraction in the gas phase was carried with temperature range 1873-2073 K for the endotherms containing 26.4% of phosphorus (FP), with ferrosilicon (grade FS 65) containing 63.8% of silicon (FS). It was first established that the ratio FS/FP (γ) influences appreciably on α_P (Table 6). In the subsequent experiences γ is equal 2.4.
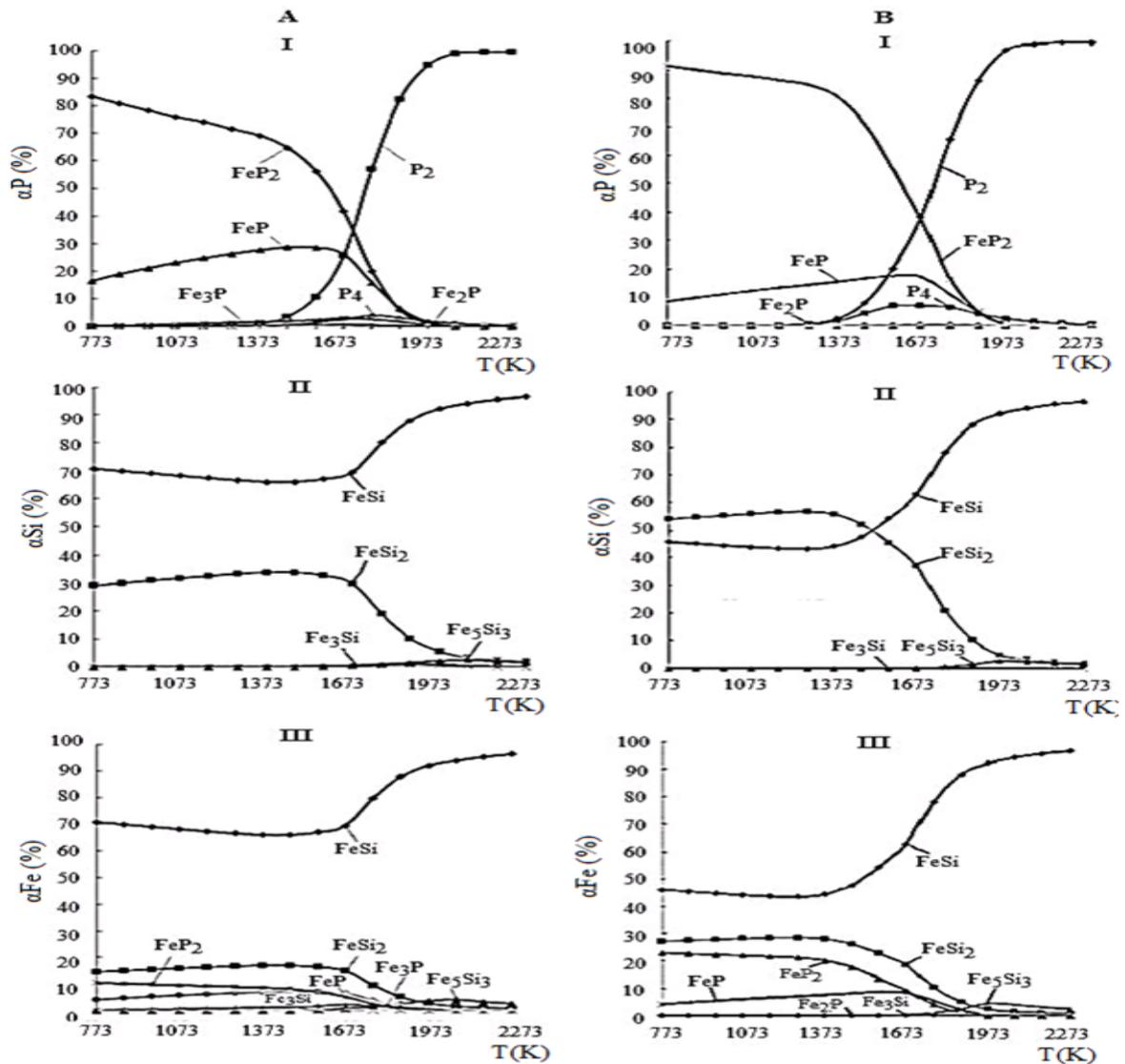
Fig. 3. Influence of temperature on the equilibrium degree of the phosphorus, silicon and iron distribution (α) in the systems $Fe_2P – FeSi_2$ and $FeP – FeSi_2$ at pressure 0.1 MPa: A – the $Fe_2P-FeSi_2$ system, B – the $FeP – FeSi_2$ system I-P, II-Si, III-Fe.

Table 6
Influence of the FS/FP ratio on α_P at the charge melting during 120 min at 1973 K

γ	1.1	1.6	1.8	2.0	2.2	2.4	2.6
α_P (%)	44.3	60.5	63.8	67.2	69.4	70.6	70.9

The information about the influence of temperature and time on α_P is given in Fig. 4.

As can be shown in Fig. 4, value of α_P as like as 80-83% could be reached at 2073 K in the course of 100-120 min. In the process, the ferrosilicon is formed with a composition of: 44.6% of Si, 48.8% of Fe, 1.7% of P, 1.9% of Mn and 3% of other minor elements (Fig. 6).
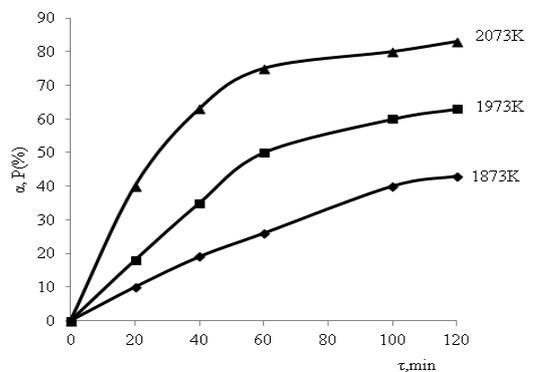
Fig. 4. Influence of temperature and time on a degree of the gaseous phosphorus formation (α_P) in the system FP – γFS at γ = 2.4.
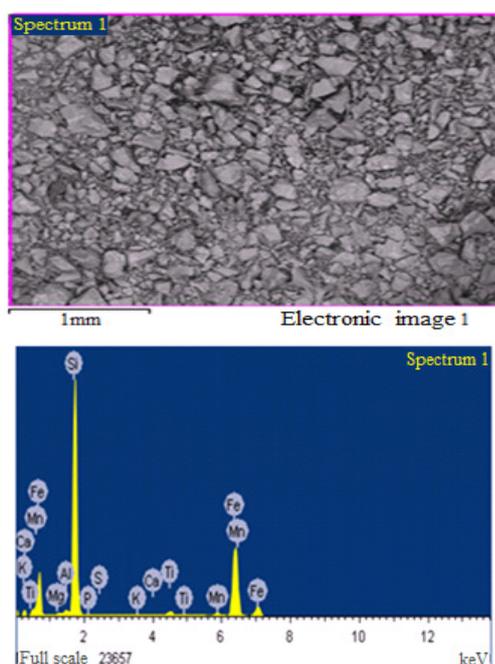
Fig. 5. Electron microscopy of the received ferrosilicon.

The applicability of the equation (Eq.5) to the process of phosphorus release from ferrophosphorus can evaluated from the plots of Fig. 6.
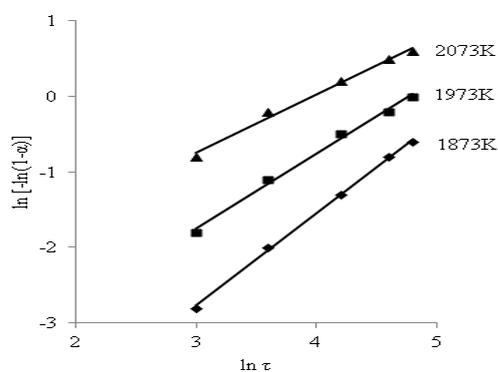
Fig. 6. Dependence $ln[-ln(1-\alpha)] = f(ln\ \tau)$ at the extraction of phosphorus from the system FP – 2.4 FS.

The influence of temperature on the coefficients "n" and "k" in the equations (Eq.5) is given on the Fig. 7. It follows from the Fig.7 that the temperature increase leads to the "n" decrease and the "k" increase. The equations of dependences $n = f(T)$ and $k = f(T)$ are the following:

$$n = 4.1554 - 0.00165 \cdot T \quad (R^2 = 0.963) \quad (Eq.17)$$

$$k = -3.5649 + 0.4729 \cdot lnT \quad (R^2 = 0.905) \quad (Eq.18)$$

Substituting the equations (Eq.17 and Eq.18) in the equation (Eq.5) we have established the generalized dependence law $\alpha = f(T, \tau)$ given in Eq.19:

$$\alpha = 1 - \exp[(3.5649-0.4729) \cdot \tau^{(4.1514-16.5 \cdot 10^{-4} \cdot T)}] \quad (Eq.19)$$

After the differentiation of the equation (Eq.19) we obtained the following expression for the phosphorus extraction rate (V), given in Eq.20:

$$V = \frac{d\alpha_p}{d\tau} = (4.1554 - 16.5 \cdot 10^{-4} \cdot T) \cdot (0.4729 \cdot \ln T -$$

$$3.5649)^{\frac{1}{4.1554-16.5 \cdot 10^{-4} \cdot T}} \cdot [-\ln(1 - \alpha1 - 14.1554 -$$

$$16.5 \cdot 10^{-4} \cdot T \cdot 1 - \alpha)] \quad (Eq.20)$$
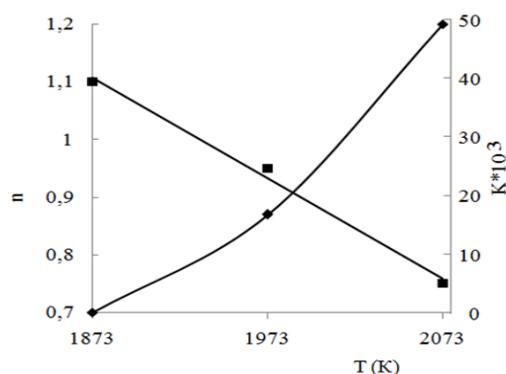
Fig. 7. Influence of temperature on the coefficients "n" and "k" in the equations (Eq.5) at the extraction of phosphorus from the system FP – 2.4 FS.

Using the equation (Eq.20) the phosphorus release rates from the system FP – 2.4 FS for $\alpha = 0.2$, 0.3 and 0.4 of parts of unity are given in Table 7.

Table 7
Influence of temperature and α_P on the phosphorus release rate (V) from the system FP – 2.4FS

Temperature (K)	V (parts of unity/min)		
	$\alpha = 0.2$	$\alpha = 0.3$	$\alpha = 0.4$
1873	0.00161	0.00146	0.00129
1973	0.0129	0.0104	0.009
2073	0.0177	0.0120	0.007

The temperature effect on V in coordinates $lgV = f(1/T)$ is presented on the Fig. 8. On the basis of this figure, using the equation (Eq.7) we detected that Eap could depends on α, reducing at the α decrease (Table 8).

Table 8
Influence of α on apparent activation energy of the phosphorus release from the system FP – 2.4FS

α (%)	20	30	40
E_{ap} (kJ/mol)	389	325	281
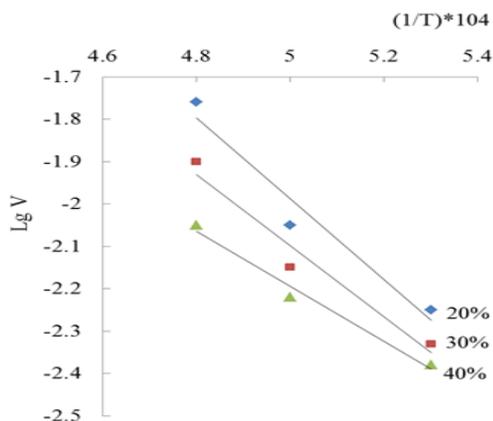
Fig. 8. Dependence $lgV=f(1/T)$ at the extraction of phosphorus from the system FP – 2.4 FS.

It follows from the determined values of E_{ap} that the process of phosphorus release from ferrophosphorus in the presence of ferrosilicon FS 65 takes place in kinetic area, and the decrease of E_{ap} at the increase of α_P is a consequence of intensification of influence of the mass exchange phenomena on the process. Nevertheless the process intensification demands the temperature increase.

Conclusions

The present study has allowed the following conclusion:

- in the system $Fe_2P–FeSi_2$ at a low temperature (773 K) there is the formation of the intermediate FeP and FeP_2, and in the system $FeP–FeSi_2$ – the intermediate FeP_2. At the increasing temperature these compounds react with $FeSi_2$ and form gaseous phosphorus (mainly as P_2);

- temperatures of initial and final stages of the phosphorus formation in the systems iron phosphides – $FeSi_2$ depends on an atomic fraction of phosphorus in the phosphides; at the increasing the mole phosphorus content from 33.3 to 50.0% the initial temperature of the gaseous phosphorus formation decreases from 1362 K to 1290 K, and a maximum degree of the transformation of phosphorus in a gaseous state decreases by 100 degrees;

- a degree of the phosphorus release from ferrophosphorus (26.4% of P) at the presence ferrosilicon (FS 65) makes 75-83% at 2073 K and duration of the process 120 min; the process is characterized by apparent activation energy from 281 to 389 kJ/mol and proceeds in a kinetic mode.

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