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INTERACTION OF TRICALCIUM PHOSPHATE WITH PRODUCTS OF CARBOTHERMIC REDUCTION OF SILICON OXIDE

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Preliminary Note – Prethodno priopćenje

The article presents the research results on the interaction of tricalcium phosphate with the products of carbothermic reduction of silicon oxide (SiO_g, SiC, iron silicides). The research was carried out by computer thermodynamic modeling using the HSC-6.0 software package. It was established that SiO_g, Si, and SiC are highly reactive towards tricalcium phosphate at relatively low temperatures. It was found that, according to the formation degree of gaseous phosphorus from $Ca_3(PO_4)_2$, silicon-containing reducing agents form a decreasing series: (SiO_g, Si)>SiC>$FeSi_2$>FeSi.

Keywords: tricalcium phosphate, carbothermic reduction, temperature, silicon oxide, thermodynamic modeling

INTRODUCTION

In blast-furnace production of cast iron, phosphorus, supplied with the charge as calcium and iron phosphates, is reduced and almost completely passes into cast iron [1, 2]. However, under certain conditions, the phosphorus transition degree from the charge into cast iron can be less and amounts to 90–94 % [3,4]. The reducing agents of phosphorus from phosphates are considered to be carbon, hydrogen, and CO [1, 5]. This statement is not entirely correct, since it was made without taking into account the effect of SiO_2 reduction products. The reduction of SiO_2 in a blast furnace can be 5-26 %, depending on the type of cast iron produced [1, 2].

According to [6], the products of SiO_2 reduction are Si, SiO_g, SiC, and in the presence of iron also FeSi, $FeSi_2$, Fe_3Si, Fe_5Si_3. The joint reduction of $Ca_3(PO_4)_2$ and SiO_2 has specific features. So, the works of Konevsky [7] found that in the $Ca_3(PO_4)_2 – SiO_2 – C$ system at a temperature of 1 400–1 500 °C the reduction rate of $Ca_3(PO_4)_2$ is ten times higher than the reduction rate of SiO_2, and at a temperature of 1 700 °C these rates are almost leveling off. Moreover, the resulting silicon is able to reduce $Ca_3(PO_4)_2$ with the formation of gaseous phosphorus. However, there is no information on the comparative reduction ability of SiO_2 reduction products with respect to tricalcium phosphate. This paper presents the results of studies of the equilibrium interaction of $Ca_3(PO_4)_2$ with Si, SiO_g, SiC, $FeSi_2$, and Fe_3Si.

MATERIALS AND METHODS

The study of the tricalcium phosphate interaction with the products of carbothermal reduction of silica was carried out using the HSC-6.0 software package developed by the Finnish metallurgical company Outokumpu [8].

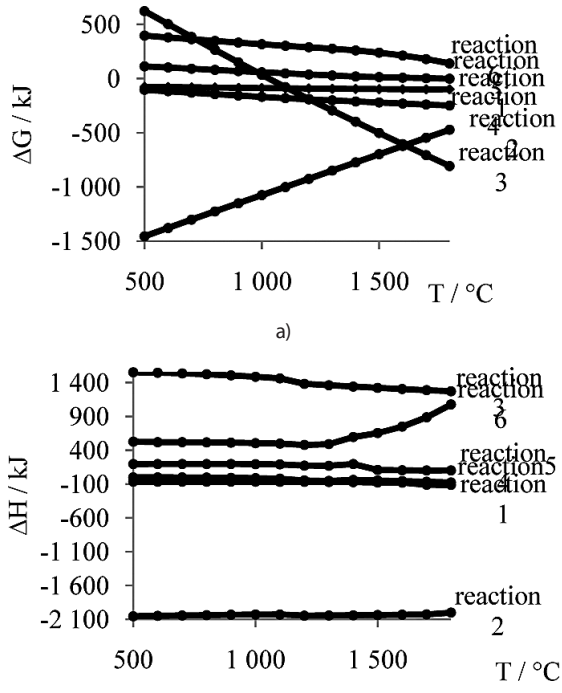

Figure 1 The effect of temperature on ΔG° (a) and ΔH° (b) for the interaction of $Ca_3(PO_4)_2$ with silicon-containing substances

At the first stage, the effect of temperature on ΔG^0 and ΔH^0 of phosphorus formation from tricalcium phosphate according to the following reactions was determined (Figure 1):

$$Ca_3(PO_4)_2+2,5Si=0,5P_{4g}+Ca_3Si_2O_7+0,5SiO_2; \quad (1)$$

$$Ca_3(PO_4)_2+5SiO_g=0,5P_{4g}+3CaSiO_3+2SiO_2; \quad (2)$$

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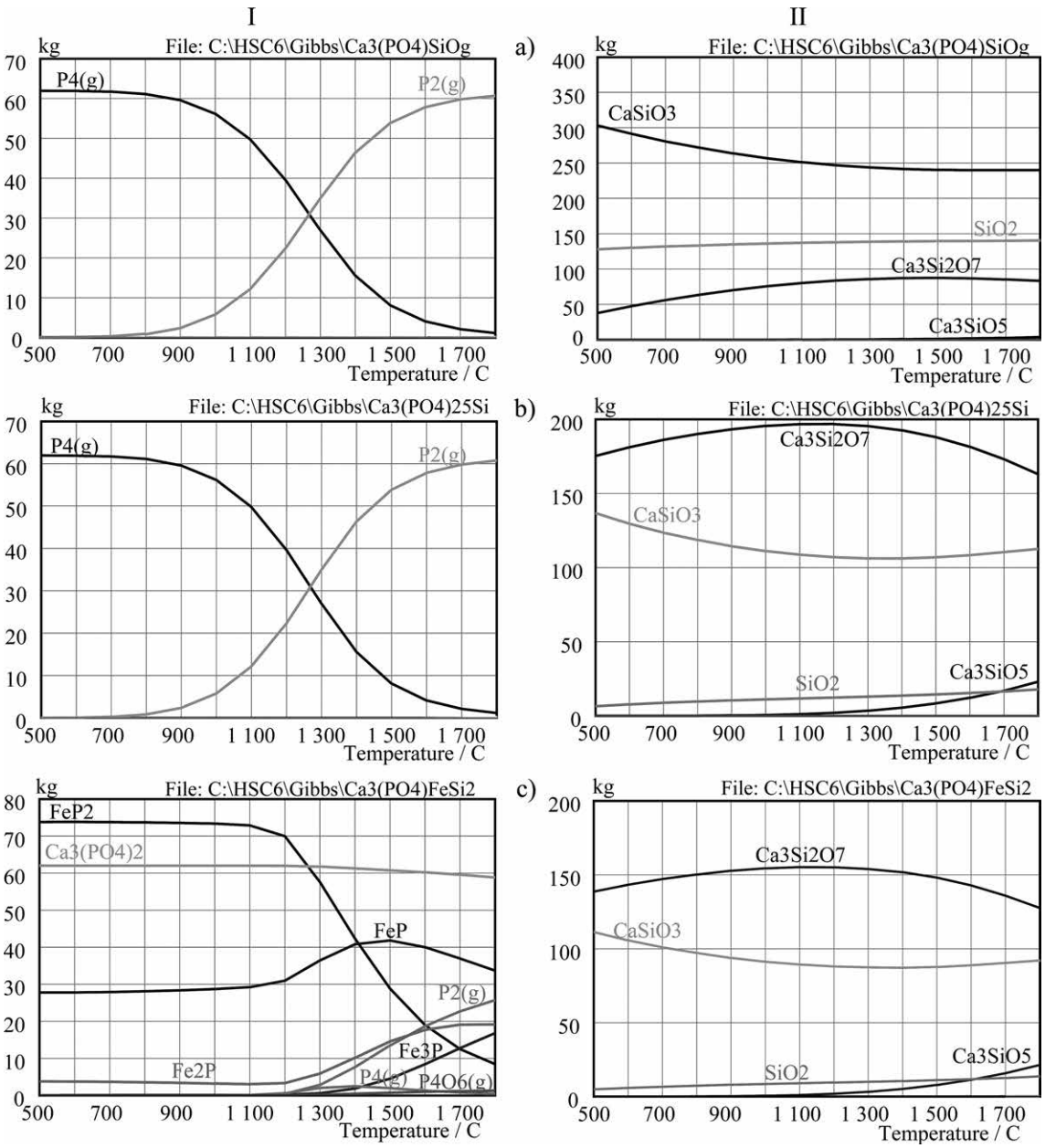

Figure 2 The effect of temperature on the quantitative (kg) distribution of phosphorus (I) and silicon (II) during the interaction of $Ca_3(PO_4)_2$ with SiO_g (a), Si (b) and $FeSi_2$ (c)

$$3Ca_3(PO_4)_2+5SiC= \\ =1{,}5P_{4g}+5CaSiO_3+4CaO+5CO; \quad (3)$$

$$Ca_3(PO_4)_2+FeSi_2=0{,}5P_{4g}+FeO+Ca_3Si_2O_7; \quad (4)$$

$$3Ca_3(PO_4)_2+5FeSi = \\ =1{,}5P_{4g}+3Ca_3SiO_5+5FeO+2SiO_2; \quad (5)$$

$$Ca_3(PO_4)_2+Fe_3Si=0{,}5P_{4g}+Ca_3SiO_5+3FeO. \quad (6)$$

It can be seen that Si, SiO and $FeSi_2$ reduce phosphorus from $Ca_3(PO_4)_2$ in the temperature range of 500-1 800 °C, silicon carbide at the temperature of more than 1 032,2 °C, and FeSi at the temperature above 1 752,4 °C. The equilibrium of reaction 6 (with the participation of Fe_3Si) is shifted to the left at 500-1 800 °C. In the $Ca_3(PO_4)_2$ – Fe_3Si system, phosphorus is not formed.

At 1 000 °C, the reduction ability of the reducing agents decreases in the series: SiO_g>$FeSi_2$>Si>SiC>FeSi>Fe_3Si; at 1 600 °C this series has the following form: (SiO_g and SiC)>$FeSi_2$>Si>FeSi>Fe_3Si. It should be noted that the reactivity of SiO_g, Si, $FeSi_2$, and SiC with respect to $Ca_3(PO_4)_2$ is higher than the reduction ability of carbon, which reduces tricalcium phosphate at temperatures above 1 496 °C. The interaction of SiO_g, Si and $FeSi_2$ with $Ca_3(PO_4)_2$ occurs with the liberation of energy, and with SiC, FeSi, and Fe_3Si – with the absorption of energy.

The second stage of the research was to determine the effect of temperature on the equilibrium distribution of elements for the interaction of $Ca_3(PO_4)_2$ with SiO_g, Si, $FeSi_2$, SiC, FeSi, and Fe_3Si. The quantitative (kg) distribution of phosphorus and silicon is shown in Figures 2, 3.

Based on these data, according to the algorithm developed by us [9], the equilibrium distribution degrees of Si,

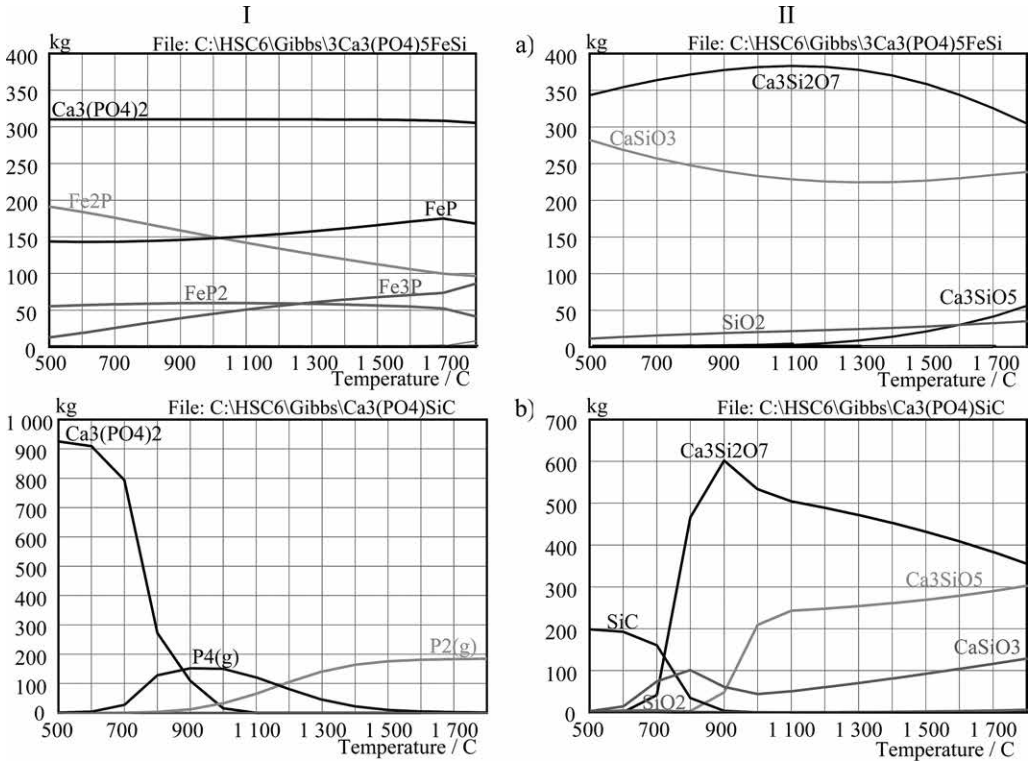

Figure 3 The effect of temperature on the quantitative (kg) distribution of phosphorus (I) and silicon (II) during the interaction of $Ca_3(PO_4)_2$ with FeSi (a) and SiC (b)

P, Fe, Ca, C, and O (%) in the systems under study were calculated and the chemical equations of $Ca_3(PO_4)_2$ interaction with Si, SiO_g, SiC, and $FeSi_2$ were determined.

RESULTS AND DISCUSSION

In the $Ca_3(PO_4)_2$ – SiO_g system, gaseous phosphorus begins to form already at 500 °C. As the temperature rises above 700 ^{0}C, the $P_{4(g)}$ molecules decompose into $P_{2(g)}$. At 1 300 °C, the interaction occurs according to the following chemical equation:

$$\underbrace{Ca_3(PO_4)_2+5SiO_g=0{,}56P_{2(g)}+0{,}2176P_{4(g)}+ +2{,}3SiO_2+0{,}297Ca_3Si_2O_7+2{,}09CaSiO_3}_{P\ (1\ 300)} \quad (7)$$

With an increase in the temperature (for example, up to 1 700 °C), the interaction between the products of reaction 7 occurs according to the equation:

$$P(1\ 300)=0{,}965P_{2(g)}+0{,}068P_{4(g)}+ +0{,}295Ca_3Si_2O_7+2{,}33SiO_2+2{,}06CaSiO_3 \quad (8)$$

In the $Ca_3(PO_4)_2$ – Si system at the temperature of ≥500 °C, the interaction is accompanied by the formation of $P_{4(g)}$, $P_{2(g)}$, $CaSiO_3$, $Ca_3Si_2O_7$, Ca_3SiO_5 и SiO_2. At 1 700 °C, the interaction occurs according to the equation:

$$Ca_3(PO_4)_2+2{,}5Si=0{,}965P_{2(g)}+0{,}017P_{4(g)}+ +0{,}6Ca_3Si_2O_7+0{,}0743Ca_3SiO_5+ +0{,}95CaSiO_3+0{,}274SiO_2 \quad (9)$$

In the $Ca_3(PO_4)_2$ – SiC system, the noticeable reduction of tricalcium phosphate begins at the temperature of more than 600 °C. At temperatures above 800 °C, the main silicon-containing product is $Ca_3Si_2O_7$. The interaction at 900 °C occurs according to the equation:

$$\underbrace{3Ca_3(PO_4)_2+5SiC=1{,}225P_{4(g)}+0{,}195\ P_{2(g)}+ +0{,}3537\ Ca_3(PO_4)_2+2{,}086Ca_3Si_2O_7+ +0{,}5245CaSiO_3+0{,}09SiC+0{,}208Ca_3SiO_5}_{P(900)} \quad (10)$$

At 1 700 °C, the products of reaction 10 interact with each other according to the equation:

$$P(900)=2{,}96P_{2(g)}+0{,}019P_{4(g)}+1{,}33Ca_3Si_2O_7+ +1{,}268Ca_3SiO_5+1CaSiO_3+0{,}07SiO_2 \quad (11)$$

In the $Ca_3(PO_4)_2$ – $FeSi_2$ system, iron phosphides (FeP_2, Fe_3P, FeP and Fe_2P) are formed at 500-1 000 °C. Then, as the temperature rises, gaseous phosphorus appears in the system. However, even up to 1 800 °C, the reduction of $Ca_3(PO_4)_2$ to $P_{2(g)}$ occurs only by 42,3 %. With an increase in the temperature, the phosphorus transition degree from $Ca_3(PO_4)_2$ into FeP_2 decreases, while in Fe_3P and Fe_2P – it increases. At 1 700 °C, the chemical interaction occurs according to the reaction:

$$Ca_3(PO_4)_2+FeSi_2=0{,}366P_{2(g)}+0{,}006P_{4(g)}+ +0{,}426FeP+0{,}106FeP_2+ +0{,}064Fe3P+0{,}134Fe2P+0{,}1921Ca_3(PO_4)_2+ +0{,}471Ca_3Si_2O_7+0{,}778CaSiO_3+0{,}2096SiO_2+ +0{,}069Ca_3SiO_5. \quad (12)$$

In the system $Ca_3(PO_4)_2$ – 5FeSi in the temperature range of 600-1 700 ^{0}C phosphorus-containing products

Table 1 **The effect of temperature on the extraction degree of phosphorus into gas / %**

System*	Temperature / °C													
	500	600	700	800	900	1 000	1 100	1 200	1 300	1 400	1 500	1 600	1 700	1 800
$Ca_3(PO_4)_2$-SiC	0,754	2,18	14,7	70,8	81,72	98,36	99,9	99,9	99,9	99,9	99,9	99,9	99,9	99,9
$Ca_3(PO_4)_2$-$FeSi_2$	<0,01	<0,01	<0,01	<0,01	<0,01	0,03	0,17	1,54	7,83	16,38	24,9	32,21	37,89	42,32
$Ca_3(PO_4)_2$-FeSi	0	0	0	0	0	0	0	0	0,01	0,02	0,04	0,013	0,056	4,69

*) In $Ca_3(PO_4)_2$ – SiO_g and $Ca_3(PO_4)_2$ – S systems at 500-1 800 °C, the phosphorus extraction degree into gas is ≥ 99,9 %

are Fe_3P, FeP, FeP_2 and Fe_2P. Gaseous phosphorus is formed at temperatures above 1 700 °C. The reaction between $Ca_3(PO_4)_2$ and FeSi at 1700 °C is described by the equation:

$$3Ca_3(PO_4)_2 + 5FeSi = Ca_3(PO_4)_2 + 2{,}01FeP + 0{,}702Fe_2P + 0{,}37Fe_3P + 0{,}445FeP_2 + 1{,}128\ Ca_3Si_2O_7 + 2{,}019\ CaSiO_3 + 0{,}5SiO_2 + 0{,}181Ca_3SiO_5 \quad (13)$$

In the $Ca_3(PO_4)_2$ – Fe_3Si system, the formation of gaseous phosphorus does not occur. At 1 800 °C, up to 60 % of phosphorus passes into the following phosphorus-containing products: Fe_2P, FeP and Fe_3P. The rest of the phosphorus remains in tricalcium phosphate.

Table 1 shows the effect of temperature on the extraction degree of phosphorus into gas as $\Sigma P_{2(g)}$ and $P_{4(g)}$.

It can be seen that SiO_g, Si, and SiC are highly reactive towards tricalcium phosphate. According to the formation degree of gaseous phosphorus from $Ca_3(PO_4)_2$, the silicon-containing reducing agents form a decreasing series: (SiO_g, Si)>SiC>$FeSi_2$>FeSi.

CONCLUSION

Based on the results obtained at the computer thermodynamic modeling of the tricalcium phosphate interaction with silicon-containing reducing agents, the following conclusions can be drawn:

- SiO_g and Si in the temperature range of 500-1 800 °C and SiC at the temperature of ≥1 000 °C reduce $Ca_3(PO_4)_2$ with the formation of ≥ 99,9 % of gaseous phosphorus;
- at the reduction of tricalcium phosphate with $FeSi_2$, the formation of phosphorus starts at 1 000 °C; the maximum reduction (42,32 %) occurs at 1 800 °C; the complete $Ca_3(PO_4)_2$ reduction does not occur due to the formation of FeP_2, FeP, Fe_2P and Fe_3P;
- in the $Ca_3(PO_4)_2$ – FeSi system, the gaseous phosphorus starts to form at the temperature of more than 1 700 °C, the maximum of this process (4,36 %) is observed at 1 800 °C; the interaction in the system is accompanied by the formation of iron phosphides FeP_2, FeP, Fe_2P and Fe_3P already at 500 °C;
- in the $Ca_3(PO_4)_2$ – Fe_3Si system, the phosphorus-containing products are FeP, Fe_2P and Fe_3P, into which up to 60 % of phosphorus passes; phosphorus in this system is not formed;
- in comparison with iron silicides, SiO_g, Si and SiC have a higher reactivity towards tricalcium phosphate. According to the formation degree of gaseous phosphorus from $Ca_3(PO_4)_2$, the silicon-containing reducing agents form decreasing series: (SiO_g, Si) >SiC> $FeSi_2$>FeSi.

Acknowledgments

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