The article presents the research results on the interaction of tricalcium phosphate with the products of carbothermic reduction of silicon oxide (SiO₂, SiC, iron silicides). The research was carried out by computer thermodynamic modeling using the HSC-6.0 software package. It was established that SiO₂, 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 Ca₃(PO₄)₂, silicon-containing reducing agents form a decreasing series: (SiO₂, Si)>SiC>FeSi₂>Fe₃Si.

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 SiO₂ reduction products. The reduction of SiO₂ in a blast furnace can be 5-26 %, depending on the type of cast iron produced [1, 2].

According to [6], the products of SiO₂ reduction are Si, SiO, SiC, and in the presence of iron also FeSi, FeSi₂, Fe₃Si, Fe₅Si₃. The joint reduction of Ca₃(PO₄)₂ and SiO₂ has specific features. So, the works of Konevsky [7] found that in the Ca₃(PO₄)₂–SiO₂–C system at a temperature of 1 400–1 500 °C the reduction rate of Ca₃(PO₄)₂ is ten times higher than the reduction rate of SiO₂, and at a temperature of 1 700 °C these rates are almost leveling off. Moreover, the resulting silicon is able to reduce Ca₃(PO₄)₂ with the formation of gaseous phosphorus. However, there is no information on the comparative reduction ability of SiO₂ reduction products with respect to tricalcium phosphate. This paper presents the results of studies of the equilibrium interaction of Ca₃(PO₄)₂ with Si, SiO, SiC, FeSi, and Fe₃Si.

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].

At the first stage, the effect of temperature on ∆G° and ∆H° of phosphorus formation from tricalcium phosphate according to the following reactions was determined (Figure 1):

\[ \text{Ca}_3(\text{PO}_4)_2 + 2.5\text{SiO}_2 = 0.5\text{P}_4 + \text{Ca}_3\text{Si}_2\text{O}_7 + 0.5\text{SiO}_2 \]  \quad (1)

\[ \text{Ca}_3(\text{PO}_4)_2 + 5\text{SiO}_2 = 0.5\text{P}_4 + 3\text{CaSiO}_3 + 2\text{SiO}_2 \]  \quad (2)
It can be seen that Si, SiO and FeSi, reduce phosphorus from Ca₃(PO₄)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 Fe₃Si) is shifted to the left at 500-1 800 °C. In the Ca₃(PO₄)₂ – Fe₃Si system, phosphorus is not formed.

At 1 000 °C, the reduction ability of the reducing agents decreases in the series: SiO →FeSi₂ >Si >SiC→FeSi>Fe₃Si; at 1 600 °C this series has the following form: (SiO₉ and SiC)>FeSi₂>Si>FeSi>Fe₃Si. It should be noted that the reactivity of SiO₉, Si, FeSi₂, and SiC with respect to Ca₃(PO₄)₂ is higher than the reduction ability of carbon, which reduces tricalcium phosphate at temperatures above 1 496 °C. The interaction of SiO₉, Si and FeSi, with Ca₃(PO₄)₂ occurs with the liberation of energy, and with SiC, FeSi, and Fe₃Si – 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 Ca₃(PO₄)₂ with SiO₉, Si, FeSi₂, SiC, FeSi, and Fe₃Si. 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,
P, Fe, Ca, C, and O (%) in the systems under study were calculated and the chemical equations of $\text{Ca}_3(\text{PO}_4)_2$ interaction with Si, SiO$_2$, SiC, and FeSi$_2$ were determined.

**RESULTS AND DISCUSSION**

In the $\text{Ca}_3(\text{PO}_4)_2$ – SiO$_2$ system, gaseous phosphorus begins to form already at 500 °C. As the temperature rises above 700 °C, the $\text{P}_4(\text{g})$ molecules decompose into $\text{P}_2(\text{g})$. At 1300 °C, the interaction occurs according to the following chemical equation:

$$\text{Ca}_3(\text{PO}_4)_2 + 5\text{SiO}_2 = 0.56\text{P}_2(\text{g}) + 0.2176\text{P}_4(\text{g}) + 2.3\text{SiO}_2 + 0.297\text{Ca}_3\text{Si}_2\text{O}_7 + 2.09\text{CaSiO}_3 \quad (7)$$

With an increase in the temperature (for example, up to 1700 °C), the interaction between the products of reaction 7 occurs according to the equation:

$$\text{P}(1300) = 0.965\text{P}_2(\text{g}) + 0.068\text{P}_4(\text{g}) + 0.295\text{Ca}_3\text{Si}_2\text{O}_7 + 2.33\text{SiO}_2 + 2.06\text{CaSiO}_3 \quad (8)$$

In the $\text{Ca}_3(\text{PO}_4)_2$ – Si system at the temperature of $\geq 500$ °C, the interaction is accompanied by the formation of $\text{P}(4\text{g})$, $\text{P}_2(\text{g})$, $\text{CaSiO}_3$, $\text{Ca}_3\text{Si}_2\text{O}_7$, $\text{Ca}_3\text{Si}_5\text{O}_5$ and $\text{SiO}_2$. At 1700 °C, the interaction occurs according to the equation:

$$\text{Ca}_3(\text{PO}_4)_2 + 2.5\text{Si} = 0.965\text{P}_2(\text{g}) + 0.017\text{P}_4(\text{g}) + 0.6\text{CaSiO}_3 + 0.0743\text{Ca}_3\text{Si}_5\text{O}_5 + 0.95\text{Ca}_3\text{Si}_2\text{O}_7 + 0.274\text{SiO}_2 \quad (9)$$

In the $\text{Ca}_3(\text{PO}_4)_2$ – 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 $\text{Ca}_3\text{Si}_2\text{O}_7$. The interaction at 900 °C occurs according to the equation:

$$3\text{Ca}_3(\text{PO}_4)_2 + 5\text{SiC} = 1.225\text{P}_4(\text{g}) + 0.195\text{P}_2(\text{g}) + 0.3537\text{Ca}_3(\text{PO}_4)_2 + 2.086\text{Ca}_3\text{Si}_2\text{O}_7 + 0.5245\text{CaSiO}_3 + 0.09\text{SiC} + 0.208\text{Ca}_3\text{Si}_5\text{O}_5 \quad (10)$$

At 1700 °C, the products of reaction 10 interact with each other according to the equation:

$$\text{P}(900) = 2.96\text{P}_2(\text{g}) + 0.019\text{P}_4(\text{g}) + 1.33\text{Ca}_3\text{Si}_2\text{O}_7 + 1.268\text{Ca}_3\text{Si}_5\text{O}_5 + 0.07\text{SiO}_2 \quad (11)$$

In the $\text{Ca}_3(\text{PO}_4)_2$ – FeSi$_2$ system, iron phosphides ($\text{FeP}_2$, $\text{Fe}_3\text{P}$, $\text{FeP}$ and $\text{Fe}_2\text{P}$) are formed at 500-1000 °C. Then, as the temperature rises, gaseous phosphorus appears in the system. However, even up to 1800 °C, the reduction of $\text{Ca}_3(\text{PO}_4)_2$ to $\text{P}_2(\text{g})$ occurs only by 42.3 %. With an increase in the temperature, the phosphorus transition degree from $\text{Ca}_3(\text{PO}_4)_2$ into $\text{FeP}_2$ decreases, while in $\text{Fe}_3\text{P}$ and $\text{Fe}_2\text{P}$ – it increases. At 1700 °C, the chemical interaction occurs according to the reaction:

$$\text{Ca}_3(\text{PO}_4)_2 + \text{FeSi}_2 = 0.366\text{P}_2(\text{g}) + 0.006\text{P}_4(\text{g}) + 0.426\text{FeP} + 0.106\text{Fe}_2\text{P} + 0.064\text{Fe}_3\text{P} + 0.134\text{Fe}_2\text{P} + 0.1921\text{Ca}_3(\text{PO}_4)_2 + 0.471\text{Ca}_3\text{Si}_2\text{O}_7 + 0.778\text{CaSiO}_3 + 0.2096\text{SiO}_2 + 0.069\text{Ca}_3\text{Si}_5\text{O}_5 \quad (12)$$

In the system $\text{Ca}_3(\text{PO}_4)_2$ – 5FeSi in the temperature range of 600-1700 °C phosphorus-containing products...
are FeP, FeP₂, Fe₃P, and Fe₅P. Gaseous phosphorus is formed at temperatures above 1 700 °C. The reaction between Ca₃(PO₄)₂ and FeSi at 1700 °C is described by the equation:

\[ 3\text{Ca}_3\text{PO}_4 + 5\text{FeSi} = \text{SiO}_2 + 2\text{FeP} + 0\text{.702Fe}_2\text{P} + 0\text{.37Fe}_3\text{P} + 0\text{.445FeP}_2 + 1\text{.128Ca}_3\text{Si}_2\text{O}_7 + 2\text{.019 CaSiO}_3 + 0\text{.5SiO}_2 + 0\text{.181Ca}_3\text{SiO}_5 \]  

(13)

In the Ca₃(PO₄)₂ – FeSi 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: FeP, FeP₂ and Fe₅P. 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 \( \Sigma P \) and \( \text{P}_{4}(g) \).

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<td>Ca₃(PO₄)₂–SiC</td>
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<tr>
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<td>&lt;0.01</td>
<td>&lt;0.01</td>
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<td>0.17</td>
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<td>7.83</td>
<td>16.38</td>
<td>24.9</td>
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<tr>
<td>Ca₃(PO₄)₂–FeSi₂</td>
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* In Ca₃(PO₄)₂ – SiO₂ and Ca₃(PO₄)₂ – S systems at 500-1 800 °C, the phosphorus extraction degree into gas is ≥ 99.9 %

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:

- SiO₂ and Si in the temperature range of 500-1 800 °C and SiC at the temperature of ≥1 000 °C reduce Ca₃(PO₄)₂ with the formation of ≥ 99.9 % of gaseous phosphorus;
- at the reduction of tricalcium phosphate with FeSi₃, the formation of phosphorus starts at 1 000 °C; the maximum reduction (42.32 %) occurs at 1 800 °C; the complete Ca₃(PO₄)₂ reduction does not occur due to the formation of FeP₂, Fe₃P, Fe₅P and Fe₅P;
- in the Ca₃(PO₄)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 FeP₂, FeP, Fe₃P and Fe₅P already at 500 °C;
- in the Ca₃(PO₄)₂ – FeSi system, the phosphorus-containing products are FeP, Fe₅P and Fe₅P, into which up to 60 % of phosphorus passes; phosphorus in this system is not formed;
- in comparison with iron silicides, SiO₂, Si and SiC have a higher reactivity towards tricalcium phosphate. According to the formation degree of gaseous phosphorus from Ca₃(PO₄)₂, the silicon-containing reducing agents form decreasing series: (SiO₂, Si) >SiC >FeSi >FeSi₂.

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