THERMODYNAMIC CALCULATION OF CARBOTHERMIC REDUCTION OF SILICON USING METHANE

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Abstract. Based on the analysis of the equilibrium thermodynamic calculation results, a range of values of the solid silicon dioxide (%m SiO₂) mass content is found for obtaining high values of the mass fractions of liquid silicon formed during pyrolysis of a condensed coal and methane gas mixture at atmospheric pressure. The calculated values of this range of the silicon dioxide mass content are consistent with the experimental data obtained.

1. Introduction
It is known that metallic silicon is produced in electric furnaces by reducing silicon dioxide with carbon. Main problems in this process are shortage, high cost and insufficient quality (low physicochemical and metallurgical properties) of the carbonaceous reducing agents, which are charcoal and its substitutes - coal and various cokes. They bring impurities into the final product, deteriorating the purity of the obtained silicon. In addition, emissions of large amounts of CO₂ into the atmosphere from the production of charcoal and coke are becoming a serious environmental concern.

In [1 - 3], experimental studies were carried out and the possibility of using methane CH₄, the main component of natural gas, for the production of silicon was shown. Methane has the best characteristics in terms of purity and reactivity comparing to the intermediate product formed during the production of silicon - volatile gaseous silicon monoxide SiO, whose escape from the furnace leads to a significant loss of silicon. The use of methane in this process could solve the problems mentioned above.

Despite numerous studies, the question of the chemical mechanism of silicon reduction, including at high temperatures, is still controversial. Under such conditions, a model experiment makes it possible to qualitatively and quantitatively investigate the process and calculate the thermodynamic equilibrium in the system.

In this work we present the results of an experimental study of silicon reduction using gaseous methane and a thermodynamic analysis of the process.
2. Experimental technique

For experimental study of the possibility of using methane to produce metallic silicon, a specially designed 130 kW DC electric arc furnace with a conductive hearth and a closed cooled roof was used. The nominal current in the experiments was 2500 A, the voltage was 50 V.

As silica-containing raw materials we used vein quartz of the Zargar deposit and quartz sands of the Dzheroi deposit in the form of briquettes. Methane acted like a carbonaceous reductant - up to 80% of the total required amount of carbon. Remaining 20% were of solid carbon, consisting of charcoal and petroleum coke [2,3]. Methane entered the furnace hearth through the upper hollow graphite electrode directly to the high temperature zone of the furnace, as shown in Fig. 1. The dissociation of CH₄ was accelerated by a nickel catalyst, which was moved along the axis of the graphite electrode by means of a metal cable and was blown by a flow of methane.

Catalyst is made in the form of a hollow nickel cylinder with a blind bottom and side holes, located in the cavity of a graphite electrode. The flow of CH₄ around the catalyst body provides a large contact area of CH₄ molecules with the heated catalyst surface, which promotes efficient dissociation of methane.

3. Thermodynamic calculations method

In this work, by means of the TDS thermodynamic code [4], we carried out thermodynamic modeling of the formation of liquid silicon from SiO₂ during pyrolysis of condensed carbon and gaseous methane at atmospheric pressure.

The method of thermodynamic calculations of complex chemical systems, implemented in the TDS code, is based on the fundamental method of extremum of characteristic functions. To describe the condensed products properties of silicon dioxide pyrolysis in mixtures consisting of condensed carbon and gaseous methane, the equation of state (EOS) of constant volume V = const was used. This EOS is used for substances with high density in the region of low pressures ~1 atm. The condensed pyrolysis products were: silicon in liquid Si(l) and solid Si(s) phases, silicon carbide SiC(s), silicon dioxide SiO₂(s), carbon C(s). The gas phase was described by the ideal gas EOS.

As a result of the calculation, all equilibrium parameters, thermodynamic properties, as well as the phase composition of the products and the chemical compositions of each of the phases present in the products are determined.

TDS is equipped with IVTANTHERMO [5] and JANAF [6] caloric properties data banks for the individual substances, containing information for several thousand substances, as well as databases with parameters of several types of thermal EOS for gas and condensed phases.

The calculations consider the pyrolysis of a homogeneous mixture of silicon dioxide and condensed coal in an atmosphere of gaseous methane, which fills the space between the solid particles of SiO₂(s) and C. It is assumed that the equilibrium thermodynamic calculation makes it possible to obtain values of the mass-average parameters and composition of pyrolysis products.
4. Results and discussion

Figure 2 shows the results of calculation of the mass amounts for the equilibrium products in the temperature range of 2200 - 3000 K with the following composition of reagents: 70 %m SiO$_2$(s), 25 %m CH$_4$, and 5 %m C(s).

It can be seen that in the temperature range $T < 2200 - 2400$ K, the initial reagents have already decomposed into gaseous products (SiO, CO, H$_2$) and condensed SiC(s). This composition of products is quantitatively retained up to 2400 K and begins to change only with an increase in temperature due to the formation of liquid silicon.

Figure 2. Equilibrium composition of pyrolysis products: 70 %m SiO$_2$(s) in a mixture of 25 %m CH$_4$ and 5 %m C(s) for $T = 2200 – 3000$ K

With a given composition of reagents (70 %m SiO$_2$(s) in a mixture of 25% m CH$_4$ and 5 %m C(s)) the maximum yield of liquid silicon is achieved at 2650 K. At this temperature, the minimum amount of SiO and maximum CO are formed, and the mass content of SiC(s) decreases to zero. At the same time, under these conditions, a significant part of silicon in the system is present in the form of gases and vapors: SiO, Si, Si,C, SiC$_2$ and Si$_2$. The mass amount of SiO does not decrease less than 18 %m.

After complete consumption of SiC (s) and reaching the maximum yield of Si(l) at 2650 K, the concentration of liquid silicon is decreasing with temperature increase. Calculations show that liquid silicon is formed during the decomposition of SiC(s). The resulting carbon is oxidized by oxygen from the decomposition of gaseous SiO. Therefore, with an increase in the mass amount of Si(l), the concentration of CO increases, and SiC(s) and SiO decreases. When silicon is formed, SiC(s) is completely consumed. This indicates its significant reduction potential, which is consistent with the results of industrial tests of silicon smelting, which were carried out in a 6.5 MW ore-thermal furnace [7]. At the same time, according to the results of calculations, the consumption of gaseous and volatile SiO is only $\sim 41\%$ of the total amount formed, and the rest of the silicon oxide $\sim 60\%$, does not enter into a reaction and leaves the reaction zone, together with the exhaust gases, which is confirmed by Katkov [8].

To obtain the dependence of the maximum Si yield on the mass content of SiO$_2$(s), we considered the range of 66 %m – 76 %m silicon dioxide mass amounts. Calculations have shown that the values of SiO$_2$(s) outside this range do not lead to an increase in the silicon content in the products; therefore, they are not presented in this work. An example of the reagents composition with a 74 %m mass fraction of silicon dioxide is shown in Table 1.

| Table 1. Composition of system with a mass fraction of SiO$_2$ 74 %m |
|---|---|---|
| SiO$_2$, %m | C, %m | CH$_4$, %m |

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For each composition of the system, a thermodynamic calculation was carried out in order to determine the amount of liquid silicon in the reaction products, see Figures 3 - 8.

| Composition | Si(l) % | CH4 % |
|-------------|---------|-------|
| 74          | 0.1     | 25.9  |
| 10          | 10      | 16    |
| 20          | 20      | 6     |
| 29.9        | 0.1     |       |

Figures 3 - 6 show that when the mass content of silicon dioxide is in the range of (66 - 76) %m SiO₂, the temperatures T_max of the maximum yield of liquid silicon are lower for compositions with a larger mass content of CH₄ than for compositions with a large mass content of C.
From Figures 3 - 8, it can be concluded that changing the mass fractions in the mixture of methane and condensed carbon in the reagents can increase or decrease the yield of liquid silicon for a given mass amount %m SiO₂.

In Figure 9 we can see the calculated dependence of the maximum mass content of liquid silicon on the mass amount of silicon dioxide 66–76 %m during the pyrolysis of SiO₂ in a mixture of condensed carbon and gaseous CH₄ for temperatures of 2200–2900 K and a pressure of 1 atm.

The line in Figure 9 consists of three sections. Sections with dashed lines 1 - 4 and 8 - 12 correspond to such mass amounts of SiO₂ in the reagents at which replacement of a part of the condensed carbon with methane does not lead to an increase in the yield of Si(l). The section 4 - 8 of the line corresponds to the mass amounts of SiO₂ in the reagents, at which the replacement of condensed carbon with methane leads to an increase in the mass yield of Si(l).

Thus, the calculations showed that replacing a part of solid carbon with methane is efficient only in range of 69 – 73 %m SiO₂. With a decrease in the amount of SiO₂ in the reagents, the yield of liquid silicon decreases: at 67 %m SiO₂ the maximum is 12.027 %m, and at 66 %m it is already 9.287 %m. The absolute maximum of liquid silicon is obtained at 75 %m SiO₂ (20.781 %m Si(l)) in a system of condensed C (coal). After this SiO₂ value, the liquid silicon yield decreases again.

The reliability of thermodynamic modeling results of the silicon formation process is confirmed by comparing it with the experimental results [2, 3]. For silicon reduction in the experiments, variants of mixed supply of gaseous CH₄ and a solid carbonaceous reductant consisting of a composition of charcoal and petroleum coke were worked out into an electricarc furnace. The main goal was to determine the optimal amount of methane gas mixed with solid carbon. A range of acceptable ratios between methane and solid carbon was established, ranging from 50/50 % to 80/20 %, within which spontaneous current surges in an electric arc furnace can be completely eliminated. Experiments have shown that when solid carbon is replaced by methane up to 80 %, the process of silicon melting in an electric furnace proceeds stably and the purity of the obtained silicon is 98.0–98.4 % [3]. With an increase in the methane content from 80 % to 100 %, the electrical resistance of the charge, due to the absence of solid carbon in it in the form of charcoal, which has a high electrical resistance, drops sharply, current surges appear and the process becomes unstable.

Thus, a series of experiments has shown the possibility of replacing solid carbon with gaseous methane up to 80 % of the total required amount of carbon to obtain Si of high technical purity.
5. Conclusion

The calculated values of the range of values of the mass content of silicon dioxide, \((66 - 76 \text{ %m SiO}_2)\), in which the maximum amounts of liquid silicon are formed, agree with the experimental data [2, 3, 7, 8].

Calculations have shown that during the formation of Si(1) intermediate products - condensed SiC(s) are consumed completely, and gaseous SiO - about 40 \text{ %m}, and the rest of it does not enter into a reaction and is lost together with the exhaust gases.

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