Thermodynamic Analysis of Interaction of Components in the SiO$_2$-C System: Improvement of Technical Silicon Production Technical Process

I. Janelidze$^1$, G. Jandieri$^2$, T. Tsertsvadze$^1$

In order to identify ways to improve the technological process of smelting metallic (crystalline) silicon of technical purity, a thermodynamic analysis of the interaction of components in the SiO$_2$-C system is carried out that reveals the main factor in obtaining high-quality technical silicon is the elimination of superposition of the silicon carbonization process that is possible by carrying out a two-stage carbothermal reduction reaction, in that firstly the incomplete reduction of silica (SiO$_2$) by solid carbon (C) is provided, accompanied by the release of new reacting gas components - SiO and CO, the subsequent interaction of which leads to the formation of the target product - technical silicon that is suitable for the production of modern solar energy converters. It is determined that main condition for highly efficient reduction reactions is the fine fractionness (< 1 mm) of the used quartzite ore with keeping of a rational temperature range for its carbothermal reduction (1688 - 2000 K). It has been shown experimentally that the optimal technical solution for the implementation of this reduction process is to perform melting in a special plasma-chemical furnace-reactor with one liquid-metal subconducting electrode, with a reverse vertical feed of the reaction gases released at the first stage. The degree of extraction of silicon was on average 95%, and the degree of its purity was 97.2%.

**Keywords:** Silicon electrocarbothermy; Thermodynamic optimization; Plasma-chemical furnace-reactor; Gasification; Reduction; Extraction.

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SiO₂-C system that would occur in the temperature range of 298 - 2000 K. For this purpose, the method of composing the three-term control of the temperature dependence of the Gibbs free energy (Δ\(G^\circ_T\)) proposed in the study [5]. All necessary initial data that are shown in Table 1, are applied from the reference literature [6-9].

Based on the analysis of reference data (Table 1) authors conclude that in the system under study in the indicated temperature range, most probably occurs the following reactions:

\[
\begin{align*}
\text{SiO}_2 + \text{C} &= \text{SiO} + \text{CO} & \text{(1)} \\
\text{SiO}_2 + \text{C} &= \text{Si} + \text{CO}_2 & \text{(2)} \\
\text{SiO} + 2\text{C} &= \text{Si} + 2\text{CO} & \text{(3)} \\
\text{SiO} + 2\text{C} &= \text{SiC} + \text{CO}_2 & \text{(4)} \\
\text{SiO} + 3\text{C} &= \text{SiC} + 2\text{CO} & \text{(5)} \\
\text{SiO} + \text{CO} &= \text{SiC} + \text{CO}_2 & \text{(6)} \\
\text{SiO} + 2\text{CO} &= \text{Si} + 2\text{CO}_2 & \text{(7)}
\end{align*}
\]

SiO + CO = Si + CO₂

(8)

The equations for the temperature variation of the Gibbs free energy of these processes would be composed based on the algebraic summation Δ\(G^\circ_T\) of the following simple reactions:

\[
\begin{align*}
\text{I.} & \quad \text{Si} + \frac{1}{2} \text{O}_2 = \text{SiO} \\
\text{II.} & \quad \text{Si} + \text{O}_2 = \text{SiO}_2 \\
\text{III.} & \quad \text{C} + \frac{1}{2} \text{O}_2 = \text{CO} \\
\text{IV.} & \quad \text{C} + \text{O}_2 = \text{CO}_2 \\
\text{V.} & \quad \text{Si} + \text{C} = \text{SiC}
\end{align*}
\]

Three-term equations of temperature variation Δ\(G^\circ_T\) of silicon oxidation reactions to SiO and SiO₂ are applied from the study [10], and for reaction III-V were obtained in this work, the sequence of calculations is given in studies [11 and 12]. Below, for the corresponding temperature limits, are stated the Δ\(G^\circ_T\) equations for the reactions I-V.
Thermodynamic Analysis of Interaction of Components in the SiO₂-C System:

\[ \text{V} \cdot \text{Si(l)} + \text{C(s)} = \text{SiC(s)} \quad /1688 - 2500 \text{ K}/ 
\]

\[ \Delta G^\circ = -29530 \pm 1300 \cdot 1.93 \cdot T \cdot \ln T + 17.12 \pm 0.18 \cdot T. \]

Table 2

<table>
<thead>
<tr>
<th>№</th>
<th>Possible reactions</th>
<th>Coefficients of equation ( \Delta G^\circ = A + B \cdot T \cdot \ln T + CT )</th>
<th>Temperatur e interval, K</th>
<th>Values of ( \Delta G^\circ ) at critical temperatures (K) cal. molec⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \text{SiO}_2\text{(s)} + \text{C(s)} = \text{SiO}_2\text{(g)} + \text{CO(g)} )</td>
<td>169690±1890 A 14.34 B 22.23 C -132.24±2.53</td>
<td>298-1688 1688-2000</td>
<td>141000 24600 24600 -100</td>
</tr>
<tr>
<td>2</td>
<td>( \text{SiO}_2\text{(s)} + \text{SiO}_2\text{(g)} = \text{SiO}_2\text{(g)} + \text{CO(g)} )</td>
<td>125150±370 A 5.72 B -63.32±1.41 C -94.58±0.28</td>
<td>298-1688 115000 49400 49200 34100</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>( \text{SiO}_2\text{(s)} + 2\text{C(s)} = 2\text{SiO}_2\text{(g)} + 2\text{CO}_2\text{(g)} )</td>
<td>141380±570 A 12.4 B -122.80±1.67 C -154.12±1.2</td>
<td>298-1688 139200 18400 18200 -10000</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>( \text{SiO}_2\text{(s)} + 2\text{C(s)} = 2\text{SiO}_2\text{(g)} + 2\text{CO}_2\text{(g)} )</td>
<td>168000±440 A 10.60 B -63.65±2.19 C -77.45±1.12</td>
<td>298-1688 94770 35410 38150 26000</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>( \text{SiO}_2\text{(s)} + 3\text{C(s)} = 3\text{SiO}_2\text{(g)} + 2\text{CO}_2\text{(g)} )</td>
<td>152020±1540 A 11.06 B -122.53±2.45 C -137.09±1.38</td>
<td>298-1688 123640 5440 7000 -18200</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>( \text{SiO}_2\text{(s)} + \text{C}_2\text{O}_2\text{(g)} = \text{SiO}_2\text{(g)} + \text{CO}_2\text{(g)} )</td>
<td>154700±1940 A 15.35 B -72.7±2.67 C -101.21±2.16</td>
<td>298-1688 112000 55700 55500 44000</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>( \text{SiO}_2\text{(s)} + 2\text{CO}_2\text{(g)} = \text{SiO}_2\text{(g)} + 2\text{CO}_2\text{(g)} )</td>
<td>82300±500 A 0.84 B -3.78±1.95 C -35.04±1.48</td>
<td>298-1688 81800 80500 80000 77400</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>( \text{SiO}_2\text{(s)} + \text{SiO}_2\text{(g)} = \text{SiO}_2\text{(g)} + \text{CO}_2\text{(g)} )</td>
<td>-44540±1580 A -8.62 B 68.92±1.04 C 66.17±1.36</td>
<td>298-1688 -30400 25000 24900 34000</td>
<td></td>
</tr>
</tbody>
</table>

Using \( \Delta G^\circ \) of reactions 1 - V, we have compiled equations for the temperature dependence of the Gibbs free energy for the desired processes 1-8, the coefficients of that are stated in Table 2. In the same Table, for the processes under study, the numerical values of \( \Delta G^\circ \) at critical temperatures are introduced that gives the possibility to us for reactions 1-8 to construct a graph of the dependences of their Gibbs energy on temperature (Fig. 1).

![Fig. 1. Diagram of dependency \( \Delta G^\circ \) of reactions 1-8 on temperature.](image)

Analysis of the nature of the stated on Fig. 1 curves gives the possibility to us to conclude the following:

1. The course of the curve \( \Delta G^\circ \) of reaction 7 clearly indicates that probability of the reduction by silica of carbon monoxide (CO) resulting in the formation of crystalline Si and CO₂ gas is insignificantly;

2. High positive values of \( \Delta G^\circ \) for reactions 2, 4 and 6, at that carbon dioxide is present in the reaction products, stipulated low probability that these processes will be practically implemented;

3. With an increase in temperature, there is a sharp decrease in the absolute values of \( \Delta G^\circ \) for reactions 1, 3, and 5, and above 1700 K they take negative values altogether that confirms the possibility of their implementation under certain kinetic conditions (for example, vacuum);

4. Separately should be outlined reactions 1 and 8. If it is possible to carry out the first stage of the reduction of silica according to reaction 1, and then on the second stage according to scheme 8, then, as a result, it is possible to obtain high-purity silicon, i.e. the main factor in optimizing the process of smelting high-purity technical silicon is to keep a rational temperature range of interaction of the reacting components, provided the maximum possible level of their gasification is ensured.

II. Experimental part

It is known that the production of technical silicon is carried out in single- or three-phase furnaces with two or three graphite electrodes, where melting is carried out mainly on high-quality quartzite (\( \text{SiO}_2 > 98 \% \)) using charcoal, petroleum coke and coal as a reducing agent [13]. For loosening the charge and reduces its sintering, but also makes it possible to replace part of the charcoal with cheaper and...
less scarce low-ash gas coal or petroleum coke. It is important to mention this, since our goal is to practically ensure the sequence of the reduction reactions with the simultaneous application of solid and gaseous reducing agents (solid carbon/carbon monoxide), according to equations 1 and 8.

An analysis of the possibilities for achieving this goal showed that a rational solution from the point of view of creating optimal temperature of reduction modes is the introduction of melting in special plasma-chemical reactor furnaces [14], where the main part of energy, similar to ore reduction furnaces, is introduced using an arc discharge. From this point of view, it is important to mention that, as it is known, the waste gases formed in the process of carbothermal smelting contain up to 80 - 85 % carbon monoxide (CO) necessary for our purpose and a large amount of finely dispersed quartz activated dust (30 - 10 g/m³). The dust and gas mixture released from the furnaces, as usual, has a temperature of 250 °C [15]. The purified waste gas from closed-type electric arc furnaces represents a high-calorific fuel with a thermal value up to 9250 - 10500 kJ/m³. Therefore currently this gas is used for heating boilers, as well as in lime kilns, as well as in the tubular furnaces for preheating the charge. The heat of the open-type furnaces exhaust gases is utilized in a steam heater with umbrella shape cooling surface.

There are some progressive researches on the application of CO for reverse purging of reaction area of the reduction smelting of manganese ferroalloys [16], but its application so far is mainly limited to an increase in the degree of dephosphorization of these alloys. In our case, reverse purging with CO gas should lead to intensification of the direct reduction reaction with obtaining high-purity silicon, without the formation of inclusions of silicon carbide.

In contrary to the mentioned development [16], where CO injection is carried out due a special lance or outlet tap-hole, in our solution, this reducing gas will be supplied due special vertical cavities of graphitized electrodes, similar to the scheme proposed in the research [17].

Especially for our purposes, according to the principle of the well-known plasma-chemical reactor with one liquid metal electrode [18], the existing laboratory single-phase electric arc melting furnace with a power of 100 kVA was modernized at our disposal.

The single liquid metal electrode reactor that is schematically presented in Fig. 2, consists from a cylindrical body, in the upper part of that is mounted, an anode unit with a starting diaphragm and a relatively short cylindrical arc chamber. The reverse polarity of the connection provides the starting unit with an increased service life. The anode unit is isolated from the rest of the structure. At the bottom of the reactor, under the open end of a special tubular double-walled arc chamber, there is a bath with electrically conductive material connected to the negative grounded clamp of the power supply. A plasma-forming gas (in our case, carbon dioxide) is supplied to the anode unit. After oscillation, the ignited arc is closed to the diaphragm, providing an indirect heating mode. With an increase in the gas flow rate, the arc is blown out from the lower end of the arc chamber and closes on the contents of the reaction bath. Due to the energy of the plasma jet and the heat released in the cathode spot of the arc, the material in the bath is heated, melted and begins to react with carbonaceous reducing agents. In order to exclude an increase in temperature in the spot of the arc to the boiling value and above, in the reaction bath, from the side pipes continuously, a pre-

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**Fig. 2.** Plasma-chemical reactor-furnace with single liquid-metal subconducting electrode: a) schematic diagram and operating principle, b) - reaction bath in the melting process (x) and c) melted technical silicon (x40).

1 - Cathode unit, 2 - starting double-walled tubular anode, 3 - reaction chamber, 4 - high-temperature arc, 5 - plasma-forming gas, 6 - processed raw material with solid reducing agents, 7 - mixture of reaction gases SiO-CO, 8 - liquid metal cathode, 9 - liquid metal anode, 10 - slag-tap-hole, 11 - metal tap hole.
Thermodynamic Analysis of Interaction of Components in the SIO₂-C System:

Table 3

<table>
<thead>
<tr>
<th>Charge material</th>
<th>Chemical composition of quartzite and mineral part of reducing agent, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiO₂</td>
</tr>
<tr>
<td>Quartzite</td>
<td>98.5</td>
</tr>
<tr>
<td>Charcoal</td>
<td>17.4</td>
</tr>
<tr>
<td>Petroleum coke</td>
<td>55.0</td>
</tr>
<tr>
<td>Coal</td>
<td>40.9</td>
</tr>
<tr>
<td>Wood chips</td>
<td>17.3</td>
</tr>
</tbody>
</table>

* Wᵢ is the moisture content in the working mass, Aᵢ is the ash on dry mass, Vᵢ is the content of volatile component.

Table 4

<table>
<thead>
<tr>
<th>Melt</th>
<th>Si</th>
<th>Al</th>
<th>Fe</th>
<th>Ca</th>
<th>Na</th>
<th>Ni</th>
<th>P</th>
<th>Mn</th>
<th>S</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>96.8</td>
<td>0.4</td>
<td>1.15</td>
<td>1.09</td>
<td>0.014</td>
<td>0.036</td>
<td>0.028</td>
<td>0.03</td>
<td>0.012</td>
<td>0.187</td>
</tr>
<tr>
<td>2</td>
<td>97</td>
<td>0.36</td>
<td>1</td>
<td>0.9</td>
<td>0.013</td>
<td>0.031</td>
<td>0.026</td>
<td>0.028</td>
<td>0.011</td>
<td>0.0184</td>
</tr>
<tr>
<td>3</td>
<td>98</td>
<td>0.3</td>
<td>1</td>
<td>0.85</td>
<td>0.011</td>
<td>0.025</td>
<td>0.020</td>
<td>0.02</td>
<td>0.08</td>
<td>0.012</td>
</tr>
</tbody>
</table>

Fig. 3. XRD spectrogram of the obtained technical silicon.

Prepared charge is fed in portions (Table 3). This eliminates the possibility of massive, premature evaporation of quartzite that also reduces the gas saturation of the reaction space of the reactor, reducing the degree of contamination of the plasma-chemical medium that is important for the productivity of the process.

In contrary to the existing designs of plasma-chemical furnaces-reactors, our scheme provides for the possibility of reverse supply of the target reaction gases - gaseous SiO and its reductant CO. Part of gaseous SiO would be condensed in the surface part of the charge, but it still remains more accessible for the CO reductant than, for example, in conventional electrocarbothermal furnaces, where CO irretrievably evaporates from the furnace throat. In addition, the achievement of the desired effect of reduction and extraction of silicon (Eqs. 1 and 8) in a modernized type furnace-reactor becomes possible due to the development and stable retention of those reaction temperature modes indicated by our thermodynamic calculations (1688 - 2000 K).

The consumption of charge materials per 1 ton of technical silicon was: 2.2 - 2.3 tons of quartzite, 1.2 - 1.3 tons of charcoal, 0.15-0.16 tons of petroleum coke and 0.2 - 0.25 tons gas coal concentrate. Specific power consumption per 1 ton of silicon with a voltage gradient in the plasma-arc column is up to 0.2 - 0.5 V/mm, averaged 12650 kWh that is up to 25 % lower than that of traditional carbothermal technologies. The chemical composition of the resulting product is presented in Table 4.

In the absence of undesired inclusions SiC in the such melted technical silicon we make sure due the results of X-ray micrography spectral phase analysis of obtained samples that is presented on the Fig. 3.

III. The main results and discussion

In the course of experimental smelting, it was found that the quantitative indicators of quartzite gasification largely depend on the surface area of its pieces (particles), i.e. - from the initial fractionation of quartz raw materials. Indirectly, this was also observed at application of quartzite from various deposits in Georgia and Ukraine (Ajameti, Kazreti, Ovruch quarry). The results of the dependence of the degree of reduction (extraction) of silicon from various deposits quartzite’s...
The dependence of the degree of silicon extraction on the fractionation of Ovruch quartzite is shown in Fig. 5. It is obvious from the diagram that an increase in the size of the fraction from 3 to 6 mm entails a decrease in the degree of reduction and extraction of silicon from 90 to 81-82%. An increase in size up to 9 mm leads to a decrease in reduction up to 70%, in the case of using quartzite with a fractionation of 12 mm, reduction drops to 60%.

Conclusions

Thermodynamic analysis of the interaction of components in the SiO₂-C system showed that the main factor for obtaining high-quality technical silicon that is possible with the exception of the possibility of superimposing an undesirable process of carbonization of silicon under reduction, is a carbothermal two-stage reduction reaction, in which first incomplete reduction of silica (SiO₂) with solid carbon (C), which results in the grain size of 0-1 mm would be completely gasified during the specified time, providing, when interacting with the CO gas reduction agent, the maximum yield of the target high-quality crystalline silicon. In this case, the degree of reduction/extraction of technical quality silicon reached 95% on average, and the degree of its purity was 97.2%.

Experimental melting of technical silicon in a plasma-chemical furnace-reactor of the proposed design showed that when recirculating the reaction (plasma-forming) gas CO₂ and keeping the optimal temperature range for the reaction of the interacting components of the fine-fraction charge by adjusting the arc power, it is possible to achieve savings in electrical energy - up to 25-30%, emissions of harmful carbon monoxide – up to 8-10 times; At the same time, the degree of reduction in the technological prime cost of production would reach an indicator of 2-2.5.
release of new reacting components in the gaseous state - SiO and CO, the subsequent interaction of that (the second stage) leads to the formation of the target metallic silicon of technical quality;

The main condition for a highly efficient electrocarbotometric reduction reaction of the indicated type is the fine fraction (<1 mm) of the applied quartzite ore with the keeping of a rational temperature range of interaction of the reacting components (1688 - 2000 K) providing the maximum possible level of their gasification;

The optimal technical solution for the implementation of this reduction process is to conduct melting in a special plasma-chemical furnace-reactor with single liquid-metal subconducting electrode, with a reverse vertical supply of the reaction gases released at the first stage;

Quartzite ore of the Ovruch deposit (Ukraine) has the highest potential for efficiency in terms of extraction and purity of smelted technical silicon.

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Термодинамічний аналіз взаємодії компонентів у системі SiO\textsubscript{2}-C: вдосконалення технологічного процесу виробництва технічного кремнію

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З метою виявлення шляхів удосконалення технологічного процесу виплавки кристалічного кремнію технічної чистоти, проведено термодинамічний аналіз взаємодії компонентів в системі SiO\textsubscript{2}-C, який вказав, що основним фактором отримання високоякісного технічного кремнію є виключення накладення процесу карбонізації кремнію, що можливо проведенням двостадійної карботермічної реакції відновлення, коли спершу забезпечується неповне відновлення кремнезему (SiO\textsubscript{2}) твердим вуглецем (C), що супроводжується виділенням нових реагуючих газових компонентів - SiO і CO, подальша взаємодія яких призводить до утворення цільового продукту - технічного кремнію, придатного для виробництва сучасних перетворювачів сонячної енергії. Встановлено, що основною умовою високоефективного проведення процесу відновлення є дрібна фракційність (< 1 мм), застосування кварцитової руди, з підтримкою раціонального температурного діапазону для її карботермічного відновлення (1688 - 2000 К). Експериментально показано, що оптимальним технічним рішенням здійснення пропонованого відновного процесу є проведення плавки в спеціальній плазмохімічній піч-реакторі з єдиним рідкометалічним струмопровідним електродом, із зворотною вертикальною подачею реакційних газів, що виділяються на першій стадії. Ступінь вилучення кремнію в середньому складав 95 %, а ступінь його чистоти - 97.2 %.

Ключові слова: електрокарботермія кремнію; термодинамічна оптимізація; плазмохімічна піч-реактор; газифікація; відновлення; екстракція.