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Thermodynamic Analysis of Interaction of Components in the SIO₂-C System: Improvement of Technical Silicon Production Technological Process

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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 performt 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.

Introduction

Metallic (crystalline) silicon of high purity, as is known, has a leading position among the semiconductor materials applied for the production of modern photoconverters [1, 2].

The durability of made from it photoconverter (solar battery) largely depends on the purity of silicon (solar quality - Si ≥ 99.99 % by weight). In turn, the purity and prime cost of solar silicon depends on the quality of applied for its production of technical, electrocarbothermal silicon (Si – 95 – 98 % [3]).

Electrocarbothermal reduction of silicon from silica in modern arc electrothermal melting furnaces practically do not represent a particularly problematic task, however, the necessity to minimize the accompanying processes of

carbonization of reduced silicon [4] determines the relevance of additional theoretical and experimental studies in this area.

Based on the above mentionre, the aim of this study is to improve the electrocarbothermal technology for smelting silicon from silica by a complete thermodynamic analysis of the reacting components (SiO_2, C) and identifying significant factors (modes) for its optimization, ensuring the highest possible reduction of metallic (crystalline) silicon with minimal formation of carbide impurities - SiC.

I. Theoretical part: research methodology

Based on the above stated, we carried out a thermodynamic analysis of the reactions expected in the

Table 1

The initial data required to assess the possibility of silica recovery by carbon (1 Cal = 4.184 Joule)

Element, Compound	$-\Delta H_{298}$ kcal·mole^{-1}	$S^o_{298,}$ cal.mole^{-1} к$^{-1}$	T_m, K	λ_m kcal· mole^{-1}	Coefficients of equation $Cp=a+bT+cT^{-2}$ cal·mole^{-1}.K^{-1}			Temperature interval K	Cp(L) cal·mole^{-1} K^{-1}
					a	b·10^3	c·10^{-5}		
C	-	1.372±0.015	-	-	5.841	0.104	7.59	298-4000	
Si	-	4.5±0.02	1688	11.9±0.2	5.72	0.59	0.99	298-1680	6.12 (1688-2871)
O$_2$	-	49.0±0.01	-	-	7.16	1.0	0.4	298-3000	
CO	26.42±0.05	47.22±0.01	-	-	6.79	0.98	0.11	298-2500	
CO$_2$	94.05±0.03	51.07±0.01	-	-	10.55	2.16	2.04	298-2500	
SiO	24.70	50.54±0.02	-	-	7.14	-	-	-	
SiO$_2$	217.72±0.34	10.0±0.10	2001	1.84	13.38	3.68	3.45	289-2000	
SiC	15.8±1.1	3.97±0.02	-	-	12.14	0.47	11.76	298-3260	

SiO$_2$-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 (ΔG^0_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:

$$SiO_2 + C = SiO + CO \qquad (1)$$
$$SiO_2 + C = Si + CO_2 \qquad (2)$$
$$SiO_2 + 2C = Si + 2CO \qquad (3)$$
$$SiO_2 + 2C = SiC + CO_2 \qquad (4)$$
$$SiO_2 + 3C = SiC + 2CO \qquad (5)$$
$$SiO_2 + CO = SiO + CO_2 \qquad (6)$$
$$SiO_2 + 2CO = Si + 2CO_2 \qquad (7)$$

$$SiO + CO = Si + CO_2 \qquad (8)$$
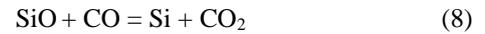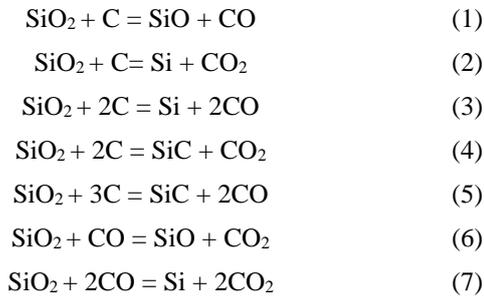
The equations for the temperature variation of the Gibbs free energy of these processes would be composed based on the algebraic summation ΔG^0_T of the following simple reactions:

I. $Si + 1/2\ O_2 = SiO$

II. $Si + O_2 = SiO_2$

III. $C + 1/2\ O_2 = CO$

IV. $C + O_2 = CO_2$

V. $Si + C = SiC$

Three-term equations of temperature variation ΔG^0_T of silicon oxidation reactions to SiO and SiO$_2$ 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 ΔG^0_T equations for the reactions I-V.

I.^{I} $Si_{(S)} + ½\ O_{2(G)} = SiO_{(G)}$ /298 - 1688 K/

$$\Delta G^0_T = - 23640\ (\pm 1500) + 6.73 \cdot T \cdot lgT - 41.75\ (\pm 1.06) \cdot T$$

I.^{II} $Si_{(L)} + ½\ O_{2(G)} = SiO_{(G)}$ /1688 - 2000 K/

$$\Delta G^0_T = - 34930\ (\pm 1700) + 7.94 \cdot T \cdot lgT - 39.0\ (\pm 1.02) \cdot T$$

II.^{I} $Si_{(S)} + O_{2(G)} = SiO_{2(S)}$ /298 - 1688 K/

$$\Delta G^0_T = - 218670\ (\pm 340) - 4.62 \cdot T \cdot lgT + 58.12\ (\pm 1.27) \cdot T$$

II.^{II} $Si_{(S)} + O_{2(G)} = SiO_{2(S)}$ /1688 - 2000 K/

$$\Delta G^0_T = - 234900\ (\pm 540) - 11.3 \cdot T \cdot lgT + 89.38\ (\pm 0.80) \cdot T$$

III. $C_{(S)} + ½\ O_{2(G)} = CO_{(G)}$ /298 - 2500 K/

$$\Delta G^0_T = - 25340\ (\pm 50) + 2.99 \cdot T \cdot lgT - 32.37\ (\pm 0.2) \cdot T$$

IV. $C_{(S)} + O_{2(G)} = CO_{(G)}$ /298 - 2500 K/

$$\Delta G^0_T = - 93520\ (\pm 30) + 1.1 \cdot T \cdot lgT - 5.2\ (\pm 0.14) \cdot T$$

V.^{I} $Si_{(S)} + C_{(S)} = SiC_{(S)}$ /298 - 1688 K/

$$\Delta G^0_T = - 15970\ (\pm 1100) - 0.46 \cdot T \cdot lgT + 0.33\ (\pm 0.78) \cdot T$$

$$V.^{II} Si_{(L)} + C_{(S)} = SiC_{(S)} \qquad\qquad /1688 - 2500\ K/$$

$$\Delta G^0_T = -29530\ (\pm 1300) - 1.93 \cdot T \cdot lgT + 17.12\ (\pm 0.18) \cdot T.$$

Table 2

Gibbs free energy of reactions occurring in the system SiO₂ - C. (1 cal = 4.184 Joule)

№	Possible reactions	Coefficients of equation $\Delta G^0_T = A + B \cdot T \cdot lgT + CT$			Temperature interval, K	Values of ΔG^0_T at critical temperatures (K) cal. mole.⁻¹		
		A	B	C		298	1688	2000
1	SiO₂(S)+C(S) = SiO(G)+CO(G)	169690±1890	14.34	-132.24(±2.53)	298-1688	141000	24600	-100
	SiO₂(S)+C(S) = SiO(G)+CO(G)	174640±2300	22.23	-160.75(±2.02)	1688-2000		24600	
2	SiO₂(S)+C(S) = Si(S)+CO₂(G)	125150±370	5.72	-63.32(±1.41)	298-1688	115000	49400	34100
	SiO₂(S)+C(s) = Si(L)+CO₂(G)	141380±570	12.4	-94.58(±0.28)	1688-2000		49200	
3	SiO₂(S)+2C(S) = Si(S)+2CO(G)	168000±440	10.60	-122.80(±1.67)	298-1688	139200	18400	-10000
	SiO₂(S)+2C(S) = Si(L)+2CO(G)	184220±640	17.28	-154.12(±1.2)	1688-2000		18200	
4	SiO₂(S)+2C(S) = SiC(S)+CO₂(G)	109180±1470	6.18	-63.65(±2.19)	298-1688	94770	35410	26000
	SiO₂(S)+2C(S) = SiC(S)+CO₂(G)	111850±1870	10.47	-77.45(±1.12)	1688-2000		38150	
5	SiO₂(S)+3C(S) = SiC(S)+2CO(G)	152020±1540	11.06	-122.53(±2.45)	298-1688	123640	5440	-18200
	SiO₂(S)+3C(S) = SiC(S)+2CO(G)	154700±1940	15.35	-137.09(±1.38)	1688-2000		7000	
6	SiO₂(S)+CO(G) = SiO(G)+CO₂(G)	126840±1920	9.46	-72.7(±2.67)	298-1688	112000	55700	44000
	SiO₂(S)+CO(G) = SiO(G)+CO₂(G)	131780±2320	17.35	-101.21(±2.16)	1688-2000		55500	
7	SiO₂(S)+2CO(G) = Si(S)+2CO₂(G)	82300±500	0.84	-3.78(±1.95)	298-1688	81800	80500	77400
	SiO₂(S)+2CO(G) = Si(L)+2CO₂(G)	97820±700	7.52	-35.04(±1.48)	1688-2000		80000	
8	SiO(G)+CO(G) = Si(S)+CO₂(G)	-44540±1580	-8.62	68.92(±1.04)	298-1688	-30400	25000	34000
	SiO(G)+CO(G) = Si(L)+CO₂(G)	-33250±1780	-9.83	66.17(±1.36)			24900	

Using ΔG^0_T of reactions I - 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 ΔG^0_T 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).
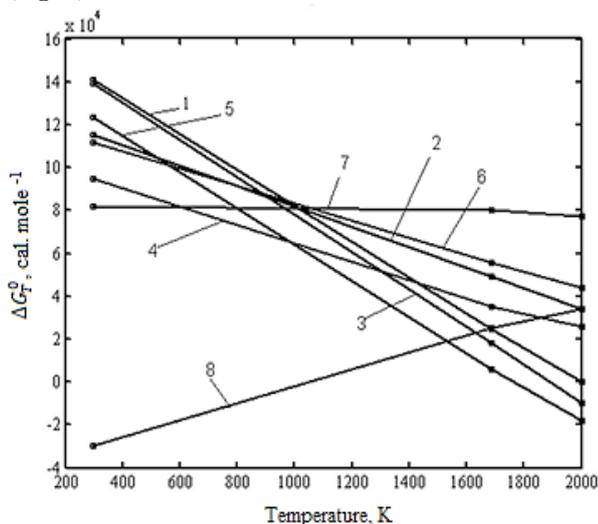
Fig. 1. Diagram of dependency ΔG^0_T of reactions 1-8 on temperature.

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 ΔG^0_T 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 ΔG^0_T 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 ΔG^0_T 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 (SiO₂ > 98 %) using charcoal, petroleum coke and coal as a reducing agent [13]. For loosening the ccharge in large furnaces (> 6 MVA), wood chips are usually applied. Its consumption reaches 2.5 - 3 m³ of compact mass per ton of alloy. The use of wood chips not only loosens 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 - in lime kilns, as well as - in lime burning furnaces 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-

<center>a   б   в</center>
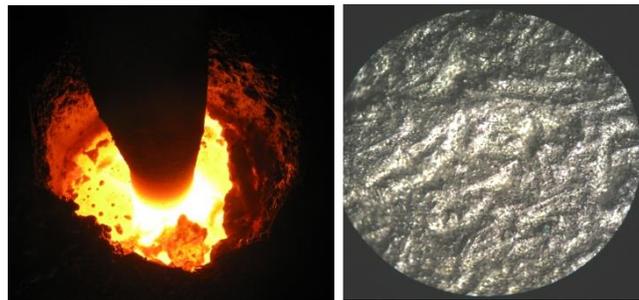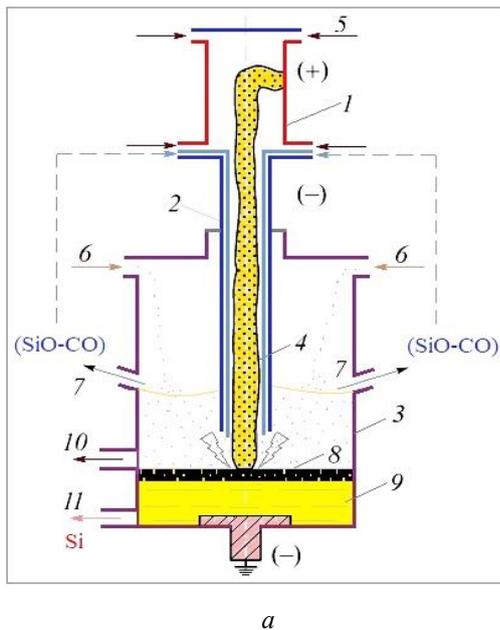
Fig. 2. Plasma-chemical reactor-furnace with single liquid-metal subconducting electrode: *a*) schematic diagram and operating principle, *b*) - reaction bath in the melting process (x) and *c*) melted technical silicon (x40).
1 - Cathode unit, 2 - starting double-walled tubular anode, 3 - reaction chamber, 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.

Table 3

Average data of the chemical composition of the charge components applied for smelting technical silicon*

Charge material	Chemical composition of quartzite and mineral part of redusing agent, %									
	SiO_2	Fe_2O_3	CaO	Al_2O_3	MgO	TiO_2	C_s	W^p	A^c	V^r
Quartzite	98.5	0.4	0.3	0.6	-	-	-	-	-	-
Charcoal	17.4	1,5	57.0	4.3	6.3	-	71	9.4	1.5	18.5
Petroleum coke	55.0	11.2	17.0	3.6	6.0	-	85.5	3.1	0.5	12.1
Coal	40.9	15.9	1.8	32.3	0.44	-	56	4.5	4.3	36.4
Wood chips	17.3	1.5	57.0	4.4	6.3	-	10.5	36.9	1.8	54.2

* W^p – is the moisture content in the working mass, A^c – is the ash on dry mass, V^e – is the content of volatile component.

Table 4

Chemical composition (%) of melted technical silicon

| Melt	Si	Al	Fe	Ca	Na	Ni	P	Mn	S	Ti
1	96.8	0.4	1.15	1.09	0.014	0.036	0.028	0.03	0.012	0.187
2	97	0.36	1.1	0.9	0.013	0.031	0.026	0.028	0.011	0.0184
3	98	0.3	1	0.85	0.011	0.025	0.020	0.02	0.08	0.012
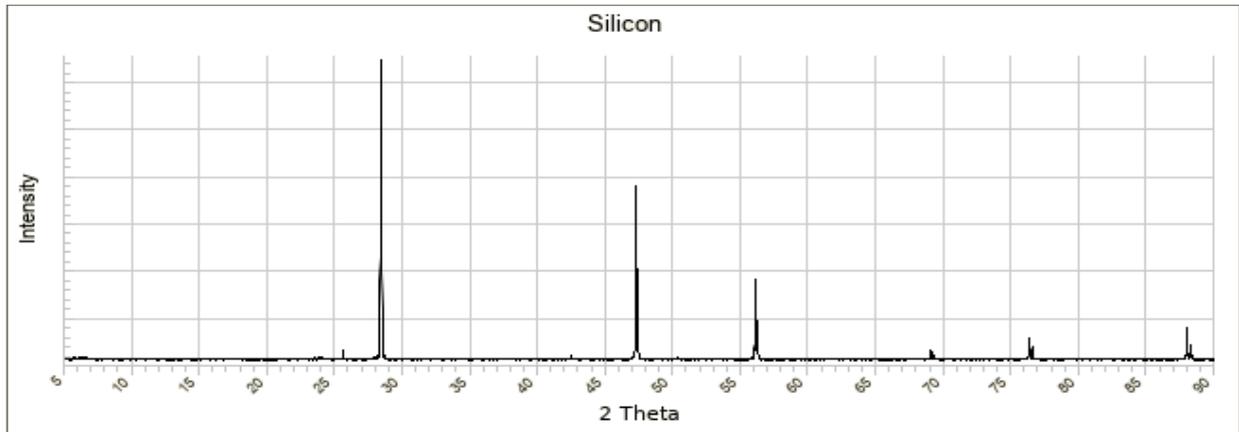
Fig. 3. XRD spectrogram of the obtained technical silicon.

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 condense 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 kW/h 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 un-desired 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
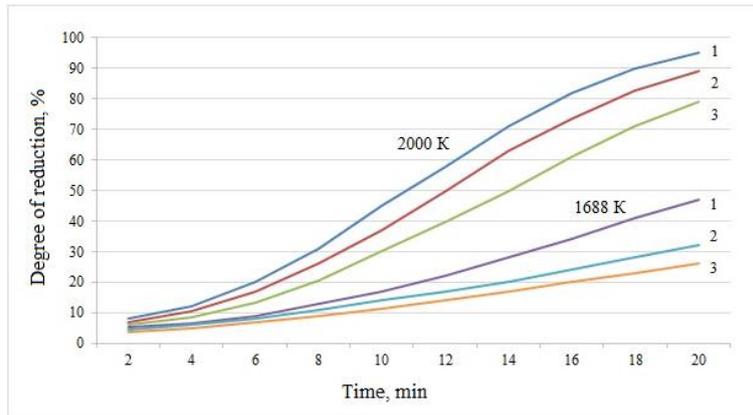
Fig. 4. Dependence of the degree of silicon reduction from quartzites of various deposits on the interaction temperature and holding period. 1 - Ovruch quartzite; 2 – Kazreti quartzite; 3 – Adjameti quartzite.
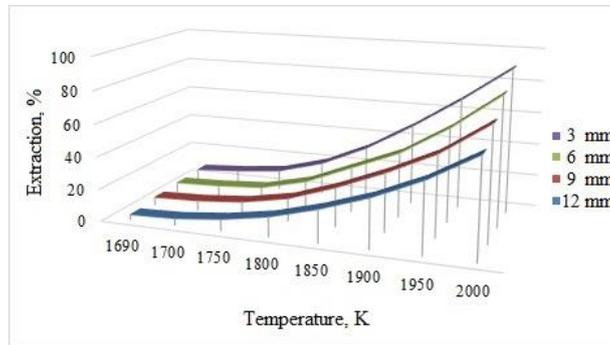

Fig. 5. Dependence of the degree of silicon extraction on the fractionation of Ovruch quartzite.

on temperature and holding period are shown in Fig. 4. In turn, the dependence of the degree of silicon extraction on the fractional content of the most efficient in terms of the degree of silicon reduction (90 %) from the Ovruch deposit quartzite is presented in Fig. 5.

It is obvious from the diagram that at increase in the size of the fraction from 3 up to 6 mm entails a decrease in the degree of reduction and extraction of silicon from 90 up to 81 - 82 %. An increase in size up to 9 mm leads to decrease in reduction up to 70 %, in the case of using quartzite with a fractionation of 12 mm, reduction drops to 60 %.

From the stated graphical dependences, it follows that dimensions of quartzite particles determine the rate of the silicon reduction process. The finer is the quartzite, the faster it interacts with carbon. The presence of smaller particles of quartz ore facilitates the diffusion conditions for the components of the SiO_2-C reaction system.

Researches have also shown that the presence of active spots on the quartzite surface (edges, angles vertexes, dislocation outcrops, pores) reduces its thermal stability and increases the rate of its gasification ($SiO_{(G)}$).

Experiments have shown that gasification of Ovruch quartzite of 1 - 3 mm fraction under a plasma arc begins at approximately 1670 K (18 - 20 K below the calculated 1688 K). At this temperature, quartzite loses approximately 15 % of its mass within 60 minutes. With an increase in temperature, the gasification rate approximately doubles for every 100 K. Quartzite with a

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 CO_2 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.

Conclusions

Thermodynamic analysis of the interaction of components in the SiO_2-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 (SiO_2) with solid carbon (C), which results in the

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 electrocarbotemic 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$_2$-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$_2$-C, який вказав, що основним фактором отримання високоякісного технічного кремнію є виключення накладання процесу карбонізації кремнію, що можливо проведенням двохстадійної карботермічної реакції відновлення, коли спершу забезпечується неповне відновлення кремнезему (SiO$_2$) 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 K). Експериментально показано, що оптимальним технічним рішенням здійснення пропонованого відновного процесу є проведення плавки в спеціальній плазмохімічній печі-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.