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USE OF NEW SOLID CARBON-CONTAINING REDUCING AGENT IN THE PRODUCTION OF TECHNICAL SILICON

Gulnara Ulyeva[1], Irina Volokitina[2]

[1] *"Arcelor Mittal Temirtau" Corporation, 101400*
Republic av. 1, Temirtau, Kazakhstan
[2] *Rudny Industrial Institute, 111500, 50 let Oktyabrya str. 38*
Rudny, Kazakhstan
E-mail: irinka.vav@mail.ru

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ABSTRACT

Technology for obtaining a solid carbon-containing reducing agent - rexyl from unmelted long-flame coals of the Shubarkol deposit was proposed. The possibility of rexyl usage is proved in electrothermal processes of technical silicon production. This application completely or almost completely excludes expensive charcoal from the charge composition.

Keywords: special coke, rexyl, silicon reduction reaction, silicon melting, thermoelectric method.

INTRODUCTION

Currently, quartz and quartzites are used for crystalline silicon production by electrothermal method. Higher requirements are imposed on the chemical composition of raw materials for silicon production than on raw materials to produce aluminum-silicon alloys. This is explained by the fact that the electrothermal reduction of silicon is a slag-free process. Oxides of other elements available in raw materials during ore reduction melting are partially reduced and transferred to silicon, contaminating it, and most importantly, they form slags of different composition. When even relatively small amounts of slag are formed, the process is extremely difficult, and its technical and economic indicators deteriorate sharply [1 - 5].

Many scientists were engaged in processes of silicon reduction from ore materials. For example, P.V. Geld believed that quartzite reduction involves not only carbon, but also the reaction product - silicon which provides the development of branched chain interaction, and justified the idea of intermediate formation of silicon oxide according to the scheme [6]:

$$SiO_2\ (sol)\ (liq) + Si\ (sol) = 2SiO\ (int) \qquad (1)$$

The process according to this scheme takes place due to the liquid state of silicon alloy which flows well around the pieces of quartzite.

In [7] P.V. Geld offers the following scheme of reduction to silicon:

$$SiO_2 \xrightarrow{Si} SiO \xrightarrow{C} Si,$$

that is, the reduction of silica in the production of high-silicon alloys passes through the intermediate formation of SiO.

According to J.V. Dashevsky and S.I. Khitrik, the reduction of silica is carried out by carbon, silicon and silicon carbide according to the scheme [8]:

$$SiO_2 \xrightarrow{C,Si,SiC} SiO \xrightarrow{C,SiC} Si.$$

F.S. Maron suggests the following scheme, which results in the formation of an intermediate product of the reaction - silicon carbide [8]:

$$SiO_2(l) \xrightarrow{\text{evaporation dissociation}} SiO_2(\text{steam});$$

$$SiO_2(g) \xrightarrow{C} SiC \xrightarrow{SiO_2,SiO} Si$$

According to V. P. Yelutin, up to 1800°C the main process is the formation of SiC as a result of direct interaction of carbon with SiO_2 through the intermediate stage of sublimation SiO_2 with the formation of the vapor phase and its subsequent adsorption on graphite. At temperatures > 1800°C, the interaction of SiC with SiO_2 with the formation of Si and SiO in the gas phase prevails. Sublimation of SiC occurs at temperatures > 2000°C [8].

The above overview shows that there are many options for the interaction mechanism in the Si-C-O system. Any of the above mechanisms of reduction of silicon from silica by carbon does not deny that the reduction process always goes through the formation of intermediate gaseous SiO, which, rising up, can be trapped in the pores of reducing agent that leads to an increase in the recovery of silicon.

Melting of crystalline silicon is a slag-free process that is possible only with pure raw materials. Even a small amount of slag 2 - 3 % of melted alloy mass significantly complicates the process and deteriorates the quality of silicon [9, 10]. So, the main requirement for quartz used as raw material for melting crystalline silicon is its purity in terms of harmful impurities - aluminum, iron, calcium, titanium oxides and other elements that contribute to lower melting temperature of quartzite and accelerate its transition to cristobalite and reduce its thermal stability. This leads to cracking and splintering of quartzite, reduction of recovery rate and deterioration of melting in the electric furnace.

Thus, minerals with high silica content, practically free of harmful impurities and well reduced in the electric furnace, are suitable to produce pure silicon. Raw material most suitable for melting technical silicon in an electric furnace is quartzite: a type of rock consisting of densely packed quartz grains (sand) cemented by clay or siliceous cement. Compaction of the particles is so significant that the distinction between quartzite grains and cement disappears [11].

Quartzite is massive, dense and homogeneous. It has volumetric apparent porosity up to 1.2 %, low water absorption (0.1 - 0.5 %), density is 2.66 g cm^{-3}, the temperature of its intensive expansion is not lower than 1150°C, hardness is ~7. Harmful impurities are concentrated in the cement that fills the voids (clay, earth, waste rock, etc.). SiO_2 content in quartzite must be at least 98 %.

Large-crystal quartz with a density of 2.59 - 2.65 g cm^{-3} and melting point of 1750 - 1760°C is also used for silicon melting. At present it is rarely used due to its scarcity.

Pure quartz sands can also be used to produce high-grade silicon. This will give some relief to the raw material issue in silicon production. There is no need for charcoal when melting briquettes. Low ash hard coal can be used as a reducing agent. Briquetted charges consisting of fine quartz sand and hard coal provide higher performance than lumpy quartzite melting and reduce the harmfulness of production [12].

A distinctive feature of the production technology of crystalline silicon that meets GOST requirements is the mandatory use of charge materials with a maximum concentration of carbon and silicon oxide. The content of unavoidable impurities, accompanying minerals of quartz and ash reducing agents (coke, coal, etc.), oxides of aluminum, iron, calcium, phosphorus should be minimized.

As mentioned above, the main requirement for raw materials for melting crystalline silicon is its purity in terms of the content of harmful impurities (oxides of aluminum, iron, calcium, etc.). Raw materials containing at least 98 % silica are required to produce a quality alloy. In addition, quartz and quartzites used to melt technical silicon must have sufficient processability determined by a set of physical properties, structural features and chemical activity. In Kazakhstan, there are 5 enterprises engaged in the extraction of quartz and quartzite for industrial applications.

The material most suitable for use as a reducing agent is rexyl obtained by thermo-oxidative carbonization of enriched coal from the Shubarkol deposit.

The purpose of the research is to determine the application of rexyl, a new type of solid reducing agent manufactured by “Armak 1” LLP (Kazakhstan), in the production of silicon and to evaluate its efficiency for the validation of new material.

EXPERIMENTAL

For experimental research on the technology of crystalline silicon production we used quartz from the “Aktas” deposit in fractions of 10 - 25 mm in order to determine their suitability. Quartz from “Aktas” deposit is characterized by its fractional and chemical

Table 1. Quartz chemical composition, %.

SiO_2	Al_2O_3	FeO	CaO
99.81	0.18	ND	ND

Table 2. Chemical composition and properties of carbonaceous reducing agents.

Parameter	Petroleum coke	Charcoal	Rexyl
Technical analysis			
Volatile content, %	7.13	10.000 ÷ 20.000	1.00 - 3.50
Ash content, %	0.29	1.500 ÷ 4.000	2.00 - 5.00
Humidity, %	4.20	6.200	< 4.00
Sulphur content, %	0.58	0.002	0.4
Structural strength, %	64.30	39.000	72.00 - 75.00
Reaction capacity at 1273 K, $cm^3/(g\times s)$	0.42	8.100	4.00 - 8.00
Specific electrical resistivity, Ohm ×cm, at: 600°C	7.31	10.010	5.48
1600°C	0.45	1.320	3.67
Ash chemical composition			
SiO_2	46.30	2.000 - 5.000	48.06
Al_2O_3	24.30	3.000 - 14.000	18.62
CaO+MgO	10.50	35.000 - 60.000	4.78
Fe_2O_3	14.20	1.000 - 5.000	7.32
P_2O_5	0.24	3.000 ÷ 5.000	0.46
K_2O+Na_2O	0.13	15.000 - 17.000	3.11
TiO_2	n/s	n/s	1.02

composition as a high-quality primary material.

A study of mineralogical and chemical composition of these quartz samples taken in different areas of the deposit showed that they have a high degree of purity (the sum of impurities does not exceed 0.18 %) and thus fully meet the requirements of silicon production. Quartz chemical composition is shown in Table 1.

A representative quartz sample was subjected to technical sampling operations for technological and scientific research. Process samples for electrothermal melts to produce crystalline silicon were selected by applying three times quarting and mixing. For other scientific and technical purposes (for chemical analysis), a sample was obtained after 13 times quarting with intermediate mixing.

Table 2 shows the physical and chemical characteristics of reducing agents used in the melting of technical silicon.

Electric silicon melting place is 200 kVA ore-thermal furnace. Existing pilot unit is designed to simulate the processes of ore electrothermia and is a single-phase ore-thermal furnace with a submerged arc and a transformer capacity of 200 kVA.

The unit makes it possible to simulate with high reliability the reduction processes taking place in industrial orethermal furnaces designed to melt a wide range of alloys, including alloys of silicon, chromium, manganese, nickel, titanium, aluminum, complex alloys, etc.

Two furnace transformers connected in parallel provide 200 kVA of power at a maximum voltage of 49.5 V and a current load of up to 4 kA. The electric furnace is equipped with four steps of secondary voltage regulation - from 18.5 to 49.5 V. Arc discharge temperature is 2500ºC - 4500ºC. The furnace has two electrodes 200 mm in diameter, and the lower electrode is rigidly fixed in the base made of conductive ramming (carbon bottom mass). The upper electrode is fixed in the copper contact jaw placed on the current-insulated suspension. Moving the electrode in the vertical plane is carried out manually through a gearbox. Electric mode control is carried out through an ammeter connected to the high side [11].

The furnace bath is fixed, one tap-hole, equipped with a graphite block. The furnace is of open type and equipped with an exhaust hood located 700 mm from the upper cut of the furnace body. The process gas exhaust system is equipped with a cyclone and a bag filter for dust collection.

Raw materials are crushed to optimum particle size and fines < 20 mm before ore-recovery melting. Most of the impurities are on the surface of quartz and quartzite pieces in the form of clay admixtures, calcium-containing crusts, dusty sediments and brittle inclusions, and the quartz crushing must be combined with water washing in order to remove them.

Quartz or quartzite for melting into technical silicon comes in pieces 20 - 80 mm in size which must have a certain mechanical strength [11].

The electric furnace was heated for 12 hours. Feeding of charge materials and treatment of furnace mouth were carried out with wooden scoops and staves. Melting in the furnace is continuous, with periodic loading of charge materials as they are melted. Melting products are discharged periodically, every 2 hours.

The furnace bottom is made of conductive electrode mass; the lining is made of fireclay bricks. The plane of furnace bottom has a slope of 5 - 7º in the direction of tap-hole which provides easier metal exit from the recovery zone. A burning system with a 30 mm diameter graphite electrode is installed to open the tap-hole.

A fundamental feature of crystalline silicon melting is intensive sintering of the charge in the zones of its heating (upper zones of the mouth). It is caused by the fact that in this area of the furnace during silicon melting a number of exothermic reactions occur, the products of which are liquid phases. During these reactions, the mouth is heated, and the charge is strongly sintered. This reduces the gas permeability of the charge and prevents it from flowing into the reaction zone. To maintain optimal conditions for the process, we had to periodically perform forced lowering of the charge into the reaction zone. The grate was treated with wooden staves, and then the next load of the charge was made. In order to avoid heat loss during charge loosening, the mouth processing operation was reduced to a minimum (3 - 5 min) with a frequency of 35 - 40 min.

In general, the process of melting crystalline silicon using new charge materials was characterized by deep electrode fit and stable current load. The charge was uniformly heated by the reaction gases creating optimal conditions for the development of the reduction process. No serious deviations from the normal melting mode were observed. During the normal process, the opening of tap-hole was made with a wooden stave. The charred tapered wooden plug was punched directly into the reaction zone. After the opening of the tap-hole, the electrode was lowered in order to increase the pressure on the reduced metal and accelerate the release process. The reaction zone was characterized by a high temperature (white heat), the metal came out actively. If necessary, wooden rods were used to poke the tap-hole.

The objectives of the pilot campaign were to:

1. Experimentally establish the optimal ratio of Shubarkol coal and rexyl in the reducing part of the charge.
2. Study furnace behavior when using a charge consisting of two components - quartz and rexyl (without hard coal).
3. Evaluate the feasibility of complete eliminating wood chips from the charge composition.

Table 3 shows physical and chemical characteristics of charge materials used in melting of technical silicon [13].

The experimental campaign consisted of the following stages (Table 4).

- Base period: melting of technical silicon of standard grades using charge mixture (charcoal+hard coal+chips+quartz) used at "Silicium Kazakhstan" LLP.
- Development of the charge mix without charcoal and wood chips by replacing them with rexyl and hard coal, respectively (rexyl share of 60 % by C_{sol}).
- Development of the charge mix with an increased proportion of rexyl (up to 80 % by C_{sol}).
- Withdrawal of hard coal from the charge mix and development of 2-component charge mix (quartz and 100 % rexyl).

Table 3. Characteristics of charge materials for melting technical silicon.

Name	Ash chemical composition, %						Technical analysis, %			
	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	P_2O_5	C_{sol}	A^d	W^p	V^d
Quartz	97.69	0.49	0.23	0.99	0.11	0.004	-	-	0.49	-
Charcoal	3.80	2.40	10.80	26.70	18.30	2.300	78.40	2.88	6.34	18.87
Rexyl	48.06	7.32	18.62	2.00	2.78	0.460	94.34	4.03	1.64	1.63
Coal shub.	57.25	17.13	21.42	1.72	2.00	0.320	48.79	1.80	7.76	41.65

Table 4. Technical and economic parameters of the pilot campaign.

Parametrs	Test period			
	1 (basic)	2	3	4
Charge, kg: Quartz	10.0	10.0	10.0	10.0
Charcoal	3.8	-	-	-
Rexyl	-	3.0	4.1	5.1
Coal shub.	3.3	4.0	1.6	-
Chips	3.3	-	-	-
Silicon recovery rate , %	77.0	81.0	91.0	76.0
Capacity, kg/hour	2.7	2.9	3.3	2.5
Average silicon content , %	96.5	97.2	97.8	96.4
Specific power consumption, MW·h/t	15.53	16.34	14.95	16.84

RESULTS AND DISCUSSION

In general, the process of melting technical silicon during the base period proceeded without significant deviations from the normal mode. There was a satisfactory fit of electrodes at a stable current load. Fluctuations in the current load were observed 1 - 1.5 hours after release, when metal was accumulated in the furnace. The current load leveled off after metal release, mouth processing and loading a new batch of charge. The charge was uniformly heated by the reaction gases which created favorable conditions for the development of reduction processes. At the same time, sintering of the mouth was observed when working with the given charge that caused difficulties in charge descending and pulling it down.

During the base period, about 300 kg of quartz was processed, and 116.0 kg of metal was obtained. The average composition of metal was as follows, %: Si - 96.5; Al - 1.20; Fe - 1.65; Ca - 0.14. According to GOST 2169-69, the obtained metal corresponds to the technical silicon grade Kr3. Extraction of silicon averaged 77 % during the campaign.

At the end of the base period the furnace was switched to a new charge. Charcoal and wood chips were completely removed from the charge. Instead they were replaced by rexyl and an additional amount of long-flame charcoal in the ratio of C_{sol} 60 and 40 %, respectively (2nd test period).

After switching to a charge without charcoal and wood chips, the following changes in furnace operation were noted:

- sintering of charge on the furnace mouth was reduced;
- the process temperature increased, resulting in an increase in the size of the reaction crucible;
- the number and intensity of blowholes on the furnace mouth decreased;
- metal at the releases was hotter.

In general, these features can be characterized as positive because the improved charge flow and increased melting space due to an increase in process temperature led to increased productivity of the furnace. Analysis of production parameters for the mentioned period showed that productivity and silicon extraction rate increased by 12 % and 7 %, respectively, as compared to the previous period.

During the period considered, 180 kg of quartz was processed and 65.7 kg of metal containing an average of 97.2 % silicon was obtained. The silicon recovery rate was about 81 %.

According to the test program, the next stage of the experimental campaign was to work with an increased proportion of rexyl in the charge batch (3rd test period). According to preliminary calculations, the share of rexyl and coal in the reducing part of the charge was 80 and 20 % C_{sol}, respectively.

Increasing the share of rexyl in the charge batch resulted in improved process performance and increased key production indicators.

In the prior period, the electrode fit was sometimes unstable, with current load fluctuations and short circuits. After switching to a charge with an increased proportion of rexyl, these phenomena were almost eliminated. Fluctuations of current load were observed only in the final period of melting (15 - 20 min before release), when metal was accumulated in the bath.

Also, after switching to the new charge, the process temperature increased. This led to an expansion of the crucible and, therefore, an increase in productivity. If during operation on a standard charge with chips the average weight of metal was 4 - 5 kg per release, in this stage this value reached 7.6 kg. The degree of silicon extraction increased by 17 % and averaged 91 %. Improved silicon utilization rates had a positive effect on metal quality: the average silicon content rose to 97.8 %.

The final stage of the experimental campaign was the development of the charge mixture without hard coal (the 4th test period).

During the first hours of the furnace operation with new charge we noticed a significant deterioration of the melting process. The mouth began to sinter intensively, and that led to formation of blowholes and overgrowth of the crucible. The current load was destabilized, and this led to violation of the electrode fit and cooling of the furnace bath. There was a decrease in the productivity of the furnace and difficult metal release from the tap-hole due to overgrowth of the discharge channel.

Extended operation with an unstable current load and loose electrode fit can lead to an emergency operation of the furnace with the need to penetrate it. Therefore, after 8 hours since new charge was put in, coal and wood chips were added to the charge. Normalization of the main parameters with an improvement in the furnace performance was noted 4 hours after the change in charge. The composition of the charge in the final period of tests corresponded to the basic.

Table 4 shows that the highest process values were achieved in the third test period, when the ratio of rexyl and coal in the charge was 80 and 20%, respectively. The main role of hard coal, as we know, is to loosen the mouth and create conditions for the uniform release of reaction gases formed in the furnace mouth [13].

If the gas permeability of mouth layer is insufficient, excessive pressure is created in the space under the mouth. As a result, accumulated gas bursts through the mouth in the form of local bursts of hot gas which leaves the reaction space at high velocity. Gas heated to high temperatures contains a significant amount of silicon monoxide SiO. Therefore, the formation of blowholes on the mouth surface not only leads to increased thermal wear of technological equipment, but also causes high losses of silicon in the exhaust gases.

Excessive gas permeability of the mouth, which corresponds to the formation of through channels in mouth layer, is also extremely undesirable. In this case, conditions are not created for sufficiently complete absorption of silicon monoxide which leaves the reaction zone unhindered without interacting with the reducing agent. This is confirmed by the results of furnace operation in the base period, when the presence of excessive amounts of wood chips and hard coal led to a decrease in the main parameters due to high gas permeability of the mouth.

Thus, favorable conditions for reductive reactions can be achieved only with a certain fraction of the opening material in the charge composition. As the tests showed, for rexyl and long-flame coal the optimal ratio (according to C_{sol}) is as follows: rexyl 80 %; coal 20 %.

Possible reasons for the deterioration of melting performance when working on rexyl without hard coal may be the following:

- sintering of the mouth and the disturbance of its gas permeability led to increased losses of silicon with the exhaust gases;
- reducing the total electrical resistance of the charge due to the removal of hard coal which has the highest

value of the resistivity among the components of carbon part of the charge composition. High conductivity of rexyl may have caused a disturbance of the electrode fit and, consequently, the furnace mouth may have become cold;

- increased segregation of quartz and rexyl due to large differences in bulk weight.

In general, the process of melting crystalline silicon using the new reducing agent was characterized by deep electrode fit and stable current load. The charge was uniformly heated by the waste reaction gases creating optimal conditions for the development of the reduction process. The reaction zone was characterized by high temperature, the metal released actively. The structure of the alloy is dense, without cavities and foreign inclusions.

Optimal technological parameters of the process were established. Replacement of traditional reducing agents by rexyl is accompanied by a significant decrease in specific energy consumption, increase in the productivity of the furnace. Analysis of technological parameters of electric melting of silicon in 200 kVA orethermal furnace showed that replacement of traditional reducing agents with rexyl is accompanied by a significant increase in productivity of the furnace, reduction of specific electricity consumption, provision of the silicon obtained in relation to such impurities as iron, aluminum, calcium.

The chemical composition of obtained metal meets the requirements [14]. The metal of the individual releases was characterized by a high concentration of silicon (Si - 98.82 %, Al - 0.38 %, Fe - 0.40 %).

Test results of the new type of reducing agent confirmed the efficiency of rexyl, the possibility of forming a two-component composition of reducing agents in the carbon part of the charge consisting of rexyl and Shubarkol coal for melting technical silicon, containing 94.57 - 98.82 % Si.

CONCLUSIONS

Mechanisms of reduction of silicon from silica by carbon always go through the formation of intermediate gaseous SiO which can be retained in the pores of the reducing agent, resulting in an increase in the degree of silicon extraction.

At present, the improved technology of rexyl production is accepted for implementation at "Armak 1" LLP.

The fundamental possibility of using rexyl (up to 80 % by C_{sol}) in the carbon part of the charge as a basic reducing agent that can replace charcoal in the charge compositions for silicon production is established.

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