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SILICON PRODUCTION USING LONG FLAMING COAL AND IMPROVEMENT OF ITS QUALITY INDICATORS

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The object of this study is to explore possibility of metallothermic producing of crystalline silicon using various types of carbon reducing agents as a reducing agent. The experience of existing enterprises shows that one of the best carbon reducing agents qualifying silicon electric melting technology is charcoal. On the other hand, charcoal has a number of disadvantages, such as its scarcity, high cost and low mechanical strength. Experimental melts has shown the principal possibility of producing the crystalline silicon that meets the requirements of quartz standard using low ash special coke and long-flame coal as reducing agents.

Key words: silicon, metalthermie, furnace charge, reducer, coke, electric melting, concentrate, quartzite, technology, metallurgy, iron, basicity, oxide, slag, ferroalloy

INTRODUCTION

General patterns of silica recovery using carbon can be determined by the thermodynamic analysis of Si-OC system.

The main summary reactions associated with silicon production, are:

$$SiO_2 + C = SiO + CO;$$
$$SiO_2 + 3C = SiC + 2CO \quad (1)$$
$$SiO_2 + 2SiC = 3Si + 2CO;$$
$$SiO_2 + 2C = Si + 2CO \quad (2)$$

In ideal conditions, when carbide of silicon is not stored in the furnace and silicon monoxide SiO is not volatilizating, the recovery reaction proceeds according to the last equation (2) [1].

Thermodynamic calculations show that the formation of silicon carbide and elemental silicon is possible at temperatures correspondingly more than 1 525 and 1 650 °C.

Based on kinetic studies, chemical, crystal-optical and X-ray analysis of the products of the silica and carbon interaction the determining role of intermediate compounds (silicon monoxide and silicon carbide) in the recovery process is proved. The process goes with the oxide in the gaseous state. Thus in the Si – O – C system this oxide can only be SiO.

Noticeable recovery of SiO_2 from clotted blends starts at 1 300 °C and increases to 1 450 °C.

Crystalline silicon melting is a slagless process, which is possible only using raw materials. Formation of even a small amount of slag – 2 - 3 % of the melted alloy mass complicates the process and affects the quality of silicon, that's why the main requirement to quartz, used as raw material for the melting of crystalline silicon, is its purity (it shouldn't contain such impurities as oxides of aluminum, iron, calcium, titanium, and other elements).

Quartzite's quality is not only determined by its chemical composition, but also by its physical properties. It must be a high heat resistant, porous (< 2 %), have low water absorption (0,1- 0,5 %).

So, the raw material for the production of crystalline silicon should have a certain granulated composition and contain not less than 98 % of SiO_2 and not more than 0,4 % of Fe_2O_3, 0,6 % of $A1_2O_3$, 0,25 % of CaO.

Crystalline silicon is smelted in open furnaces with a capacity from 6,5 to 22,5 MVA (megavolt-ampere) by continuous method with the constant release of the melt.

For loosening the blend in the large furnaces there is used wood split. Its consumption reaches 2,5 - 3 m of compact mass for 1 ton of the alloy. Reduction of batch sintering along with use of rippers is promoted by rotation of a tank. The batch composition is counted for 100 kg of quartzite or quartz in plenty of 10 – 15 % of the reducer against the theoretically necessary one.

Silicon is released permanently, it is caused by the need to reduce the duration of melt's stay in the furnace gas atmosphere as a result of the processes of secondary carbide formation. With an excess of reducing agent the blend is overgrowing as a result of corborundum formation (SiC) by the reaction of $SiO_2 + 3 C = SiC + 2 CO$.

While silicon is smelted up to 2 % of slag is formed. Slag contains 30 – 50 % SiO_2, 8 – 15 % SiO, 10 – 30 % Si, 10 – 40 % SiC. This slag can be used for steel deoxidation and also for smelting of ferroalloys with silicon.

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STUDY AND SELECTION OF MATERIAL FOR EXPERIMENTATION

Not all quartzes are suitable for melting of crystalline silicon, as different types of them have the same chemical composition, but they have different melting behavior in the heating process and in the recovery stage at high temperatures. These differences depend on the character and content of impurities, structure of crystalline phases and other factors determined by the genesis of the quartz. Quartz has a light color indicating low content of hematite; its cracks have hydroxides of iron and manganese membranes. Structure of quartz is coarse-grained with small closed pores, there is no cement ligament.

As starting materials there were used long-flame coal and quartz, their chemical composition is shown in Table 1, fractions 1,6 – 0,6 mm.

Laboratory researches of quartz included study of parameters such as density, water absorption and behavior during heating.

Table 1 **Chemical composition and technical analysis of materials / wt %**

Material	Quartzite	Long-flame coal	Shubarkul coal ash
A	-	2	-
V(ppp)	-	44	-
W	0,1	2,9	-
S	-	-	-
C(tv)	-	50	-
SiO2	99	-	56,9
Al2O3	0,54	-	21,3
Fe2O3	0,15	-	2,76
CaO	0,10	-	2,76
MgO	0,07	-	1,77
P2O5	-	-	0,4
SO3	-	-	3,5

Increased ability to absorb moisture is considered as a negative feature of quartz, as it can lead to destruction of water-saturated pieces of quartz because of the rapid release of steam when quartz gets on the top of the furnace, that's why water absorption is an important characteristic of quartz in terms of its technological effectiveness in melting of silicon.

Heat resistance of quartz and its behavior during heating were studied in high-temperature furnace of Tamman in the range from room temperature to 1 600 °C with heating speed of 10 °C/min. Samples of quartz are not destroyed up to 1 600 °C. Streaks of dark color begin to melt at 1 250 °C. After cooling down to room temperature the samples were cracked. Researching the thermal shock showed that the sudden increasing of temperature makes quartz samples begin to crack. During curing the same samples in the oven for an hour at a temperature of 1 600 °C, begins the formation of cracks on the boundaries of quartz blocks.

In general, research of physical and chemical properties of quartz showed that it is characterized as the primary material with good quality and meets the requirements of production of crystalline silicon.

In the production of crystalline silicon, the highest performance are achieved by using charcoal that is produced by pyrolysis of wood (oak, birch, beech, etc.) and that contains up to 20 % of volatile substances, up to 3 % of ash. Charcoal ash contains a small amount of SiO_2 (less than 5 %) and consists mainly of alkaline metal oxides (CaO, MgO, K_2O, Na_2O), which are harmful impurities contaminating metal. Charcoal has high physical and chemical properties (the reaction capacity, resistivity). Mechanical properties of charcoal are slightly lower than properties of other carbon reducing agents used in electrothermics.

Petroleum coke has a low ash content, high strength, but it is only used in combination with charcoal. Using only petroleum coke reduces technical and economic parameters and complicates the process of silicon melting. It is explained by low physical and chemical properties of petroleum coke at high temperatures. Also pitch coke has low ash content, but it has high cost.

Kazakhstan has reserves of low-ash dross-coal. Production of carbon reductants from new dross-coal allows to obtain coke having improved physical and chemical properties. Individual layers of long-flame coal with 1,3 % of ash contain 60 % of SiO_2, which is a useful in silicon alloys smelting impurity silicon alloys, and their recycling makes it possible to produce a high quality reducing agent with minimal impurities.

To obtain an active reducing agent in the form of a special coke by method of thermal-oxidative coking was launched unit for production of special coke. The specific capacity of the unit is 35 kg / hour of special coke.

For melting of crystalline silicon as a carbon reducing agent was used special coke produced by coking of long - flame coal with 10 - 40 mm fraction in layer of 100 mm at temperatures of 750 - 850 °C. Special coke's 0 - 5 mm fraction was deselected. Special coke differs from charcoal because of low ash content to be deposited in the 100 kg of carbon. Moreover, the chemical composition of the special coke's ash is also more good for silicon melting , as it has a high content of SiO_2 (58 % vs. 2 - 5 % in charcoal). Including content of SiO_2 in the special coke's ash amount of impurities in 100 kg of carbon is 1,44 %.

Special coke's reactivity is several times higher than that of petroleum coke and slightly lower than that of charcoal. Structural strength of special coke is higher than that of charcoal, but lower than that of petroleum coke.

On that bases replacement of charcoal and petroleum coke by special coke almost completely excludes these disadvantages of reducing agents. Special coke's parameters correspond physical and chemical properties of the mixture of reducing agents, which indicate a potential of replacement of two reducing agent by one special coke.

Together with coke, it was decided to use Shubarkul extra pure carbon as a reducing agent. Coals of Shubarkol deposits belong to Long-flamegaseous, they are petrographically homogeneous. The content of vitrinite is more than 80 % of the organic mass.

To obtain crystalline silicon out of quartz of Karaganda deposit a large laboratory test were made in furnace with capacity of 200 kW.

A distinctive feature of the crystalline silicon production technology is the mandatory use of blend materials with the maximum concentration of carbon and silicon oxide.

The content of the inevitable impurities that associate minerals quartzite, reducing agents' ash (coke and coal), and oxides of aluminum, iron, calcium and phosphorus should be minimized.

The process of carbon thermal recovery of silicon oxides happens according to reactions:

$$SiO_2 + C = SiO + CO \quad (3)$$

$$SiO_2 + 3C = SiC + 2CO \quad (4)$$

$$SiO_2 + 2SiC = 3Si + 2CO \quad (5)$$

$$SiO_2 + 2C = Si + 2CO \quad (6)$$

These reactions are realized according to the thermodynamic data in the temperature range of 1 650 - 1 960 °C.

EXPERIMENTAL METHOD

To perform the experimental studies of production technology development of crystalline silicon we used quartz of Karaganda deposit with 5 - 25 mm fraction. By fractional and chemical composition quartz of Karaganda deposit is characterized as high-quality primary material.

The most suitable material to use as a reducing agent is low ash special coke produced by thermooxidative firing of selectively chosen long - flame coal. Special coke's and low ash coal's faction is 5 - 25 mm.

Experiments were performed in a low pit ore-thermal furnace with capacity of 200 kW. Arc discharge temperature is 2 500 - 4 500 °C it is provided by graphite electrode with a diameter of 150 mm. Electric furnace is equipped with four secondary voltage regulation stages - from 18,5 to 49,5 V. To provide the purity of crystalline silicon, furnace hearth is made of finely floured compressed spectrally pure graphite.

The surface of the hearth is tilted 5 - 7 °C towards the hole which provides a more easy way of crystalline silicon out of reduction zone. Melting was processed by continuous method, with loading of the blend in small portions as shrinkage of furnace top, with periodic release of metal in every 2 hours.

Since the load of the blend the electrode was coming down. Quartz, loaded into the furnace during smelting, was cracking; the load increased, but remained stable at 160 - 170 A. In general, the process of melting of crystalline silicon using these burden materials was characterized by stable parameters of the furnace, deep position of electrodes and stable current load.

Burden material was heated evenly by reaction gases, creating optimal conditions for the development of recovery processes. Serious deviations from normal mode were not observed.

To minimize the possibility of additional carbide formation because of the contact of melt with graphite mold, metal pouring was made layer by layer. Fissure bullions have iron-gray color with distinct crystal slabs. Alloy structure is dense, without shells and foreign inclusions. On the surface of bullions some slag particles were observed, but their quantity was minute (less than 0,2 %). The average content of silicon for the stable period made 97 – 98 %. On the separate emissions there was recorded content of silicon to 98,7 %

The derived crystal silicon is also a raw material for producing solar silicon to which rigid requirements for the content of harmful impurity are imposed.

In this regard, along with smelting process there was proposed the method of filtrational refinement of silicon [3].

For carrying out laboratory experiments on influence research of technical silicon filtering on pollution by harmful impurity it was designed and prepared the filtering equipment with use of the computer program "Compass" and which is given on the figure 1 and consisting of three main parts: melting crucible 1 (with a hole in the botoom closed by a stopper), established directly on filtering section A which in turn is precisely put on the metal reservoir B.

Filtering elements were made of magnesite by of pelletization with use of binding and cobbed silicon dioxide [4] – Figure 1.

The mass of silicon test charge which is filled up in a melting crucible made 300 - 400 g. According to heat-

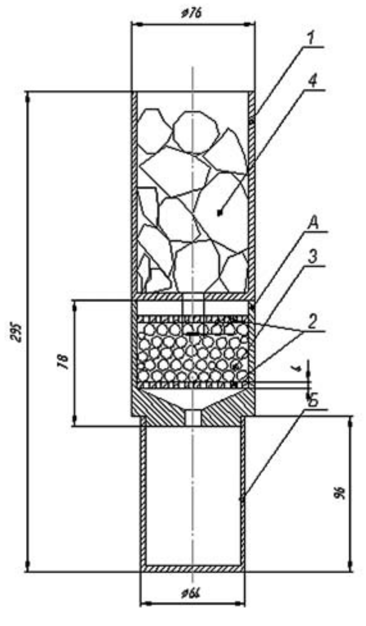

Figure 1 Assembled filtering equipment
1 - crucible, 2 - bottom and top grids, 3-filtering elements, 4 - furnace charge, 5 - metal reservoir

ing and the subsequent fusion of metallurgical silicon the filter was simultaneously heated up too. At achievement of temperature of 1 530 -1 500 °C the fusion passed via the filter in the metal reservoir B. After full cooling of the furnace there was made analysis of filtering equipment, and taken an ingot of the filtered silicon from the median part of which samples were collected for conduction of analyses.

Results of the spectral analysis show that existance of such elements as calcium, copper, lead and sulfur considerably decreased as we can see from the table 2 given below.

Table 2 **Effect of filtrational refinement of metallurgical silicon from impurity**

Silicon	Filter material	Effect of silicon refinement / % from impurity			
		Ca	Cu	Pb	S
filtered	MgO	48	31	0	0
filtered	Al_2O_3	27	24	74	0
filtered	SiO_2	61	57	62	75

CONCLUSION

On the basis of conducted studies the following conclusions can be made:

1. According to the analysis of physical and chemical processes, formation of silicon carbide is the initial reaction during production of silicon.
2. While conducting experiments on interaction of silica with coal there were obtained results which confirm formation reaction of silicon carbide at temperature of 1 500 - 1 550 °C, which is the initial reaction of silicon reduction out of silex.
3. During melting in large laboratory furnace there was obtained the metal of marks KR1, Rp2, RP3, which confirms the effectiveness and usefulness of Shubarkul's coal as a reducing agent to produce technically pure silicon.
4. Foundry casting works showed the principal possibilities of obtaining the crystalline silicon according to the requirements of standard from quartz of Karaganda deposit using new non-traditional reducing agents as recovery agents: low ash special coke and long-flame coal instead of expensive charcoal and petroleum coke.

For the first time there was experimentally established the filtration effect of refinement of metallurgical silicon from impurity elements. Thus the studied effect depends on the nature of applied filtering material. So, for example, efficiency of purification of silicon from calcium at using the magnesite and alumina filter makes respectively 48 and 27 %, and when filtering using the quartzitic filter – 60 %.

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Note: The translation of the N. M. Drag, Karaganda, Kazakhstan