UDC 669.782

N.V. Nemchinova [(1)], manager by a department, d.t.s., professor
T.V. Kritskay [(2)], manager by a department, d.t.s., professor
G.A. Kolobov, professor, c.t.s.

STUDY OF IMPURIT COMPOSITION OF SILICON METALLURGICAL BRANDS

[(1)] Federal public budgetary educational institution of higher professional education, the «Irkutsk state technical university», Russian Federation,
[(2)] Zaporozhe state engineering academy, Ukraine

The basic technological scheme for producing metallurgical silicon by carbothermal method has been considered. The chemical composition of smelted and refined products has been studied. It has been shown that the quality of silicon depends on the chemical composition of the used charge materials and further oxidizing refining. It has been found that after the additional controlled cooling the silicon's impurities are presented by intermetallide of composition as $CaSi_2(Al)$, $FeSi_2Ti(Al)$, $FeSi_2Al_{0,5}(Ca)$.

Key words: metallurgical silicon, ore-smelting furnace, refining, chemical composition, X-ray spectral microanalysis

Introduction. Technical (metallurgical) silicon, got by a carbothermic method in ore-thermal furnaces (OTF), finds a wide use at the production of alloys, semiconductor devices, in chemical industry and sun energy [1,2].

In the world there are a few plants, productive metallurgical silicon [3]. In the last years Peoples Republic of China becomes by one of serious competitors to the traditional producers. The largest plants are also located on territory of Europe: in Norway and France. Among the Asian states lately Korea develops the own production of silicon, and Kazakhstan has the government program of development of this sector of economy.

On Ukraine metallurgical silicon it was begun to produce with 1972 at the Dneprovsky aluminum plant, renamed later in ZAC (Zaporozhe aluminum combine).

In Russian Federation the production of silicon of metallurgical brands is carried out on two plants, imputing in the complement of concern «Rusal»: CAJ «Silicon» (Irkutsk area, Shelekhov) and CAJ «Sual «Silicon-Ural» (Kamensk-Ural, Sverdlovsk area.) [4]. Thus on the first plant the operation of exuding affinage is used already a long enough ago, that allows to organize the production of silicon for more wide circle of industries-consumers (fig. 1), while on the second plant this technological process is only approved and is on the stage of tests.

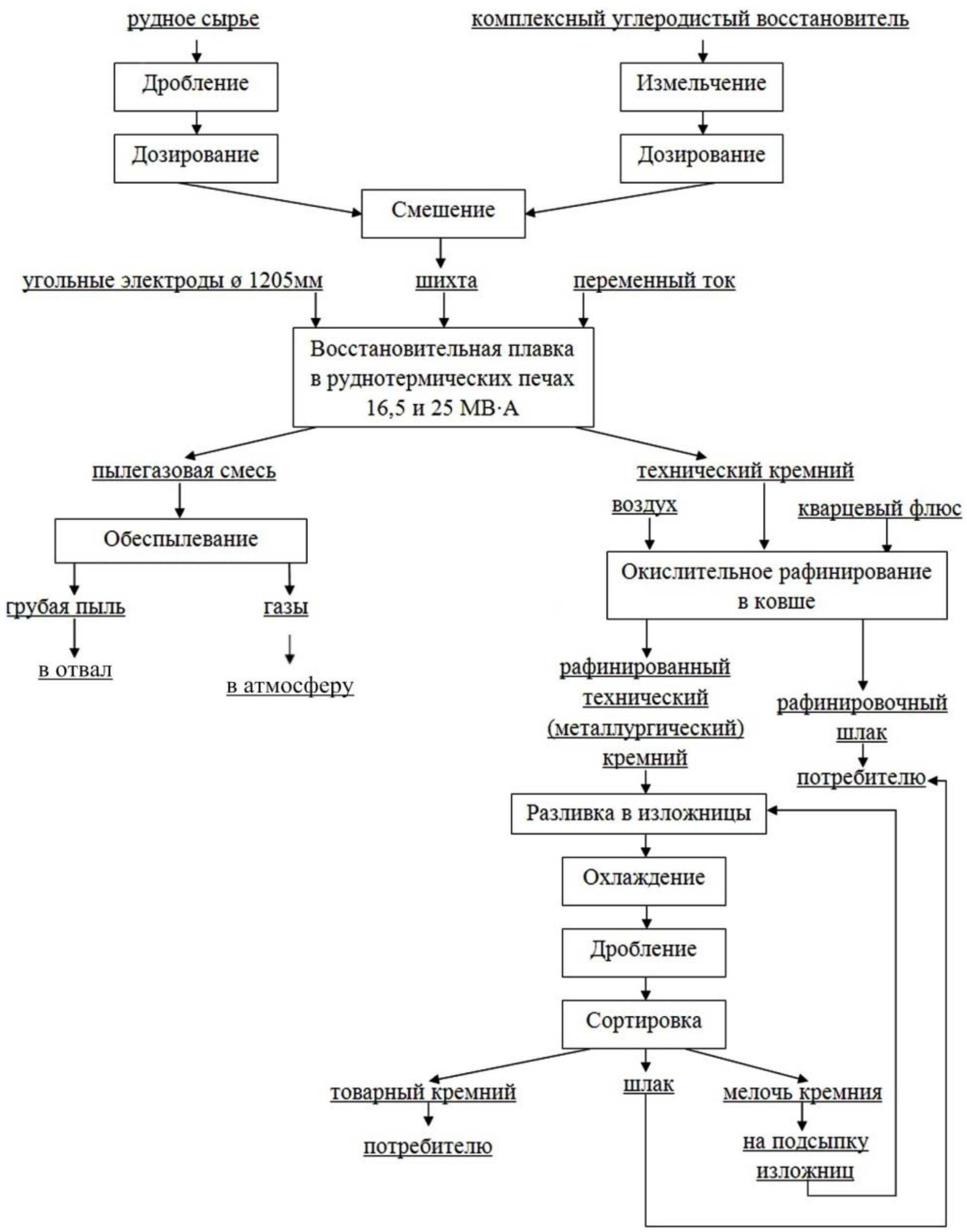


Figure 1 - Technological scheme of receipt of metallurgical silicon in ore-thermal furnaces on CAJ «Silicon»

Depending on the further use of metallurgical silicon can be used also a vacuum affinage, treatment of fusion of silicon by silicate slag's (by fusions of oxides calcium, magnesium, aluminum), extraction and acid lixiviating, gradient melting, treatment of fusion by active gases and (by the pair of water, oxygen, oxides of carbon, by a chlorine in mixture with an argon and other) normal crystallization. In particular, in silicon, used for the production of sun elements (brand of UMG) the processes of affinage must provide content of impurities within the limits of 1.0-0.1 ppmw [5].

The purpose of our researches is a study of chemical composition for silicon of metallurgical brands.

Production of silicon by a carbothermic method. The process of the carbothermic smelting of silicon in OTF can be described by the simplified reaction:

$$SiO_2 + 2C \Rightarrow Si + 2CO \quad . \qquad (1)$$

As raw material materials on CAJ «Silicon» is used quartzite of Cheremshansky deposit, which behaves to the cleanest silicon containing materials of the East region of Russian Federation, and carbon reducer, being the optimal expected composition of different carbon materials (anthracite coal, oil-coke, charcoal, arboreal wood chips). Considerable part of impurities in the smelted product is brought by ore part of charge on the average, %, accordingly: 60 aluminum, 55 iron and 9 calcium [1]. Among reducers the least low-ash is oil-coke, however from subzero reactionary ability it can not use in a carbothermic process in a singular, for what in the complement of charge for silicon smelting impute different combinations of carbon materials, including a charcoal as the most active reducer [6].

Rise of quality of silicon, smelted in OTF, possibly by the selection of high-clean raw material materials.

At melting in the high temperature areas of oil-thermic furnace there are difficult physical and chemical transformations of charge materials with formation of intermediate products: carbide of silicon and monoxide of silicon which speeds away from the area of reaction with end gas, those results in high not enough extraction of having a special purpose product [1,7].

Study of chemical composition of silicon. As productive practice shows, silicon, got on one furnace, corresponds to the different brands concordantly ГОСТ 2169-69. It is related to the considerable vibrations of chemical composition of burdening materials, imputing in process. The contents of basic product can hesitate from 96.66 to 99.05 %, and impurities in the smelted product are presented as a non-metallic (slag) - globules (low temperature quartz, leucite, mullite and other), and also as the recovered metals, constrained in intermetalides of different composition, mainly silicides.

A carbon is in silicon as carborundum or in the free state. Connection a «silicon-carbon» is very durable, a carborundum breaks only at a high temperature (higher 1700 ºC) with use SiO_{gas} and SiO_{2sol}. The accumulation of carborundum can take place at influence of surplus of reducer and decline of temperature [1,8,9].

Oxidizing affinage on CAJ «Silicon» is carried out by blowing out of fusion by air in a ladle with capacity 1.83 m^3 and capacity to 4.0 t fusion. The complex operation of cleaning is sent to the decline of content in silicon of aluminum, calcium, phosphorus, titan and row of other impurities, and also on the complete removal of the shallow and large including of slag. On a fig. 2 the results of affinage of silicon on a plant for December, 2014 (power of OTF – 16.5 MVA) are presented.

As be obvious from a fig. 2, ladle oxidizing affinage of silicon is most effectively for moving away of calcium and aluminum (due to their great affinity to oxygen, what, for example, at phosphorus). On the average, common content of silicon, produced from OTF, increases on 1,17 % for OTF-1, on 1,42 % - for OTF-3 and on 1,18 % for - OTF-6.

Depending on composition of charge materials, acting on melting, composition of refinery slag can be insignificantly varied (table 1). However on phase composition of differences not observed practically, the phases of the tangled kinglets of silicon of $Si_{(met)}$, carbide and oxide of silicon are always fixed.

Table 1 - Composition of slags after the oxidizing affinage of silicon

Test	Concentration, the mass. %						
	Fe_2O_3	Al_2O_3	CaO	$Si_{(мет)}$	SiC	SiO_2	Other impurities
1	0,54	4,9	7,7	45,4	2,2	38,4	0,86
2	0,58	3,4	4,6	56,4	2,1	30,9	2,02
3	0,61	5,2	7,2	53,7	2,9	28,4	1,99
4	0,58	2,8	7,5	67,9	0,3	18,0	2,89
5	0,41	3,5	7,2	56,6	1,1	28,6	2,59
6	0,50	4,1	8,0	52,3	3,1	31,4	0,64
7	0,57	4,8	6,6	48,5	3,0	34,6	1,93
8	0,38	4,0	5,9	60,0	2,9	24,6	2,23

After the oxidizing affinage of silicon in a ladle fusion is poured out in coal moulds (on a bottom lay the change of layer silicon a 20-50 mm), level of filling by silicon - below than brim of mould on 100 mm.

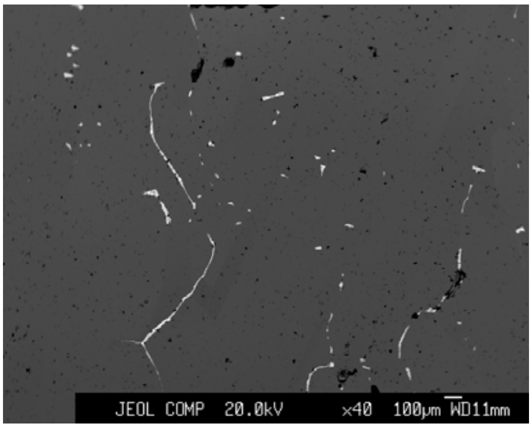
For rise quality of silicon after its cleaning in a ladle we were suggested to apply crystallization of fusion with the gradual decline of temperature.

Experiments executed in the muffle furnace LHT (firm «*Nabertherm*», Germany) at the set temperature of fusion - 1480 °C and cooling durations - 6 hours.

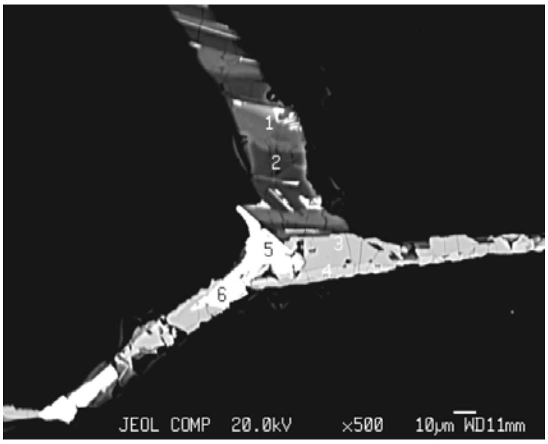
Table 2 - Chemical composition of the intermetalides including in the investigated sample

Point	*Si*	*Fe*	*Ti*	*Ca*	*Al*	*Zr*	In all
1	34.594	34.202	0.000	7.334	23.870	0.000	100.000
2	57.640	0.000	0.000	41.464	0.896	0.000	100.000
3	35.153	32.391	24.866	0.000	0.684	6.876	100.000
4	35.296	33.723	0.000	7.573	23.409	0.000	100.000
5	41.524	37.932	0.000	1.115	8.078	11.335	100.000
6	100.000	0.000	0.000	0.000	0.000	0.000	100.000

The samples of silicon after experience were analyzed by the method of X-ray spectral microanalysis (XSMA) with the use of electronic-probe microscope «JXA-8200» (Japan). Preparation of samples to researches was executed with use the cutoff machine-tool «*Labotom*-15» their polishing and buffing was carried out on the grinding-buffing machine-tool «*Tegramin*-25» of firm «*Struers*» (Denmark). Secondary electrons, emitted by a sample as a result of unresilient collisions of bunch of electrons with the atoms of target, carry information about relief of surface and allow to study morphology of objects (the so-called pictures are in SEI). Part of electrons gets to the depth of sample, disperse as a result of resilient collision with the atoms of target and go out on surface. These electrons are named back dissipated and carry information as about composition of target (COMPO-contrast on an atomic number), so on surface topographies of the studied object (TOPO-topo-graphical contrast) [10]. In table 2 and on fig.2 results over of this research are brought.



a



б

a is a general view of topography of surface, increase of x 40*;*
b is the intermetalide including (table 2), increase of x 500*.*
Figure 2 - Results of XSMA of sample of silicon after even crystallization**:**

After cooling of fusion of silicon with the controlled decline of temperature looked the even strippant of impurities to the borders of silicon grains. In most cases these impurity including is presented difficult intermetalides, mainly silicides; there were also including of carborundum. According to these tables. 2, in the investigated complex including along with actually by silicon as basis (point 6, table 2) is fix $CaSi_2$ (with the insignificant substitution of calcium on an aluminum), $FeSi_2Ti(Al)$, $FeSi_2Al_{0.5}(Ca)$. Presence of zirconium in some points it is possible to explain by the pickup of this element from the fettling of OTF at producing of silicon from notch.

Thus, at realization of the even cooling for silicon fusion the even strippant of impurities is fixed to the borders of grains with forming of the complex intermetalide including of difficult composition. The further rise quality of silicon is possible at treatment of the ground up material, for example, by acids [11,12].

Conclusions. Quality of silicon of metallurgical brands, smelted in orethermal furnaces, depends on chemical composition of the used raw material materials (sili-concontaining raw material and carbon reducers). Thus for achievement of optimal extraction of silicon it is necessary to use the combined reducer, combining materials both with a subzero ash-content (oil-coke) and with sufficient reactionary ability (charcoal).

For expansion of sphere of the use of metallurgical silicon after its smelting it is necessary to apply an affinage by cleaning of fusion blowing out by air in a ladle, reducing content of aluminum, calcium and phosphorus. For the further decline of impurities additional gradual crystallization of silicon during 6.0 hours is offered. By method of XSMA in the samples of this silicon the intermetalide including, up-diffused on the borders of grains, which have difficult composition and presented mainly by silicides, were fixed: $CaSi_2(Al)$, $FeSi_2Ti(Al)$, $FeSi_2Al_{0.5}(Ca)$. The acid methods of treatment of silicon powder are offered for their moving away.

REFERENCES

1. Выплавка технического кремния [Текст] / С. В. Архипов, А. А. Тупицын, О. М. Катков и др. – Под ред. О. М. Каткова. – Иркутск : ЗАО «Кремний», 1999. – 244 с. – Библиогр. : с.
2. Немчинова, Н. В. Кремний: свойства, получение, применение [Текст] : учеб. пособие / Н. В. Немчинова, В. Э. Клец. – 2 изд. – Иркутск : Изд-во ИркГТУ, 2008. – 272 с. – Библиогр. : с.
3. Andersen, B. The metallurgical silicon process revisited [Текст] / B. Andersen // Silicon for the Chemical and Solar Industry X: proc. of Scientific Conf. (28 June-02 July, 2010, Ålesund. – Geiranger (Norway)). – Ålesund. – Geiranger, 2010. – P. 11-23.
4. Елкин, К. С. Производство металлического кремния России – состояние и перспективы [Текст] / К. С. Есин // Сб. тезисов докладов VI Междунар. конгресса «Цветные металлы и минералы-2014» (15-18 сент. 2014 г., г. Красноярск). – Красноярск, 2014. – С. 180.
5. Критская, Т. В. Основные требования к технологическим схемам получения кремния солнечного качест-ва [Текст] / Т. В. Критская, С. Л. Нагорный, Л. Я. Шварцман // Металургія : наукові праці Запорізької державної інженерної академії. – Запоріжжя: РВВ ЗДІА, 2009. – Вип.19. – С. 72-81.
6. Немчинова, Н. В. Углеродистые восстановители для выплавки кремния [Текст] / Н. В. Нем-чинова // Электрометаллургия легких металлов : сб. научных трудов. – Иркутск, 2000. – С. 96-99.
7. Немчинова, Н. В. Распределение примесей при рудно-термической выплавке кремния [Текст] / Н. В. Немчинова, А. А. Яковлева, М. С. Леонова // Вестник ИркГТУ. – 2013. – № 12 (83). – С. 230-236.
8. Венгин, С. И. Технический кремний [Текст] / С. И. Венгин, А. Р. Чистяков. – М. : Металлургия, 1972. – 206 с. – Библиогр. : с.
9. Рагулина, Р. И. Электротермия кремния и силумина [Текст] / Р. И. Рагулина, Р. И. Емлин – М. : Металлургия, 1972. – 239 с. – Библиогр. : с.
10. Reed, S. J. B. Electron Microprobe Analysis [Текст] / S. J. B. Reed // Cambridge London. New York. – Melbourne : Cambridge University Press, 1975. – 306 p.
11. Немчинова Н. В. Исследование процесса карботермического получения кремния в электродуговых печах [Текст] / Н. В. Немчинова, С. С. Бельский, А. К. Тимофеев // Технология металлов. – 2012. – № 6. – С. 3-9.
12. Немчинова, Н. В. Повышение чистоты кремния при гидрометаллургическом его рафинировании [Текст] / Н. В. Немчинова, А. А. Тютрин // Перспективы развития производства кремния : сб. научных статей, посвященный 30-летию ЗАО «Кремний». – Шелехов : ЗАО «Кремний», 2011. – С. 83-85.