ISSN 0003-701X, Applied Solar Energy, 2014, Vol. 50, No. 4, pp. 282–286. © Allerton Press, Inc., 2014.
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Modernization of the Technology for Obtaining Technical Silicon for Solar Energy

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Received March 17, 2014

Abstract—The results of the comprehensive modernization of the technology of high-quality silicon production to provide partial or complete replacement of solid carbonaceous reducing agents with gas and the use of quartz sand with changes in technological process as raw material are described.

DOI: 10.3103/S0003701X14040045

The first phase of industrial production of technical silicon (TS) in the Navoii region [1] with a volume of 12000 tons per year and the planned 2014 commissioning of a second plant for manufacturing TS in the special Angren industrial zone in the Republic of Uzbekistan with a planned production capacity of 6000 tons per year, which is focused on vein quartz from Zargar, not only confirmed forecasts [2–4], but also spurs the development of new technical and technological solutions aimed at modernization of the carbothermic process of TC smelting, including the use of local raw materials.

Among the most pressing problems were the replacement of imported birch charcoal that is used in this process as the main carbonaceous reducing agent (CRA) and the expansion of the domestic resource base of silica sources, for example, by using local quartz sand, as well as the gradual improvement of existing carbothermic process. Developments in these areas have yielded results [5] that are interesting for practical use. Thus, within the framework of solving the problem of replacing imported birch retort charcoal, a carbothermic process for obtaining TS from the Zargar vein quartz using natural gas (CH_4) as the CRA was developed.

Table 1a,b shows the comparison of the chemical compositions of TS samples that were obtained with (a) standard CRA and with (b) natural gas.

The data from Table 1a show that with the use of TS from the domestic quartz vein made using imported charcoal as a CRA a silicon content of 98% can be obtained, which corresponds to the Kr0 type [6, 7]. However, detailed impurity analysis of the product, conducted by analogy with [5], which was obtained in several series processes that are separated in time and not limited with regard to the contents of only Fe, Ca, and Al, shows that the product may be on the edge of the lower Kr1 type. The picture changes significantly if CH_4 is used as a CRA. In this case, the purity of the product (see Table 1b), not only exceeds the requirements to the TS Kr0 type, but corresponds to Kr00 type, with purity regulated by current GOST 2169–69 at the level of 98.8% [6]. The developed technology can be recommended for the industrial production of TS and can bring significant economic benefits not only through full or partial replacement of imported CRA, but also by improving the quality of TS in terms of residual impurities and the reproducibility of this index. The latter aspect is important not only for improving the quality and yield of semi-finished products ($SiHCl_3$ or SiH_4) for subsequent chemical and metallurgical stages of production of TS, but also allows one to actually set the task of developing refining operations, thus to reform the direct metallurgical stage of the production of TS in polycrystalline or multisilicon [2, 8, 9] that is suitable for the manufacture of solar cells (SCs). The new technology does not require reworking the manufacturing equipment except for the crucible assembly and electrode (know-how), as well as the electronic systems for maintaining the modes of stable combustion of the electric arc. The latter situation is inevitable, since even a change in the type of charcoal or wood from which it is derived substantially by tens of percent to two or more times changes its electrical resistance [4, 6]. Partial, and even more so complete replacement of charcoal with CH_4, while maintaining the same stoichiometric ratio of silica and CRA in a charge, is accompanied by a significant change of both the absolute value of its electrical conductivity and the dependence of this parameter

Table 1. The chemical composition of TS that was obtained using birch charcoal (a) and methane (b) as a CRA, %

Element	Si	Al	Fe	Ca
a	98.6	0.38	0.36	0.21
b	98.89	0.2	0.1	0.11

Table 2. The chemical composition of the vein quartz from the Zargar area

a) typical data of geologists averaged over the largest veins 6, 8, 9, 12 [8]

Percentage, %			Au, grams per ton
SiO_2	Fe_2O_3	TiO_2	
99.16– 98.13	0.03–0.39	0.002–0.008	from 0 to 0.04

b) authors' data on the content of silica and impurities in it in the form of oxides, in % [5]

Fe	K	Al	Mg	Ca	Na	Cu	Cr	Mn	Ni	SiO_2
0.64	0.22	0.077	0.076	0.069	0.045	0.007	0.004	0.004	0.001	98.83

c) typical data of independent expertise

Percentage, %										
SiO_2	Al_2O_5	Fe_2O_5	CaO	MgO	K_2O	Na_2O	TiO_2	MnO	P_2O_6	Other
99.64	<0.01	0.08	0.06	<0.01	<0.01	0.02	0.00	<0.01	<0.01	0.18

on the temperature and requires the development of new rules for smelting TS. The feasibility of the proposed technology is indirectly confirmed by its high efficiency, which is identified in the related carbothermic metallurgical process of obtaining iron from ash slag in the Angren TPP, which is performed with the use of natural gas in the industrial environment of Angrenenergotsvetmet. The need to expand the resource base of TS production through the use of domestic silica sand (SS) along with vein quartz is due to the following circumstances. Specific features of the geological area [10, 11] of, for example, the Zargar vein quartz with provisionally estimated resources of 1.2 million tons, cause extremely high costs of its production, because the quartz veins are deposited among binary and muscovite granites near the tectonic contact with shales, and the strength of the veins is comparatively low. This makes the wide use of mining equipment difficult and increases the proportion of manual labor. The cost of production, which is justified if the raw material is entirely used for TS for microelectronics (especially since Zargar belongs to the category of rare, if not unique [12], ores due to the low content or even absence of the boron impurity, (Table 2)), becomes problematic when it is used only on the production of TS for the subsequent manufacture of solar cells for land and civil use. At the same time, in terms of a silica mineral resource base Uzbekistan has vast natural resources, namely more than 96 deposits of quartz sands and quartz–feldspar sands [13], whose stocks contain more than 500 million tons. The chemical and mineralogical compositions, structural features, properties and enrichment technology [13, 14], especially for the glass industry [14, 15], of the local SS are fairly well studied. SS of the Kizilkum mining region that were described in [16] with a silica content of 98–99%, which creates good prospects for their involvement in the production of TS, are of practical interest.

The use of silicon sands from a number of fields whose sands not only have high silica contents, but also have a structure of individual grains in the form of a core of silicon dioxide with a shell, in the manufacture of TS will allow one to effectively apply relatively simple and cost-effective methods for the enrichment of raw material for the removal of clay and other mineral impurities, such as sieving, sorting by size and washing. In [6], and in dozens of patents that have been analyzed in a number of works [9, 17], the use of a granulated batch in the technology of production of TS is described, i.e., pellets or briquettes that contain precleaned quartzites and CRA that are ground to the optimum size in a predetermined stoichiometric ratio. It is obvious that the use of SS is possible in this option, since simple addition of sand to charge in the standard technology [7], not to mention the complete replacement of silica in lump fractions, leads to the occurrence of a vitreous and impervious to reaction gas layer on the surface of the fusion mixture during melting and, respectively, to the breakdown of the entire process.

In [9] development of a methodology was described and the optimum parameters were determined, namely balling up of small fraction components of a fusion mixture using an alkaline environment to obtain binder granules and to ensure that they have a porous but mechanically strong structure. Use of a granular fusion mixture not only on the basis of SS, but also deliberately crushed quartz and quartzite, as well as their mixtures and the use of CRA that is also brought to the highest possible purity and optimal particle size, will raise production standards, automate the input control and operational management of raw materials, and thereby improve the quality of the smelted product. This solution is not associated with radical alterations of equipment, which, along with the obvious advantages of this technology, will facilitate its implementation. On the other hand, this technique, although it clearly has benefits in comparison with the standard method [7], cannot solve its main problems completely. Thus, the proportion of usable energy, i.e., energy that is directly used for the reduction reaction of SiO_2 [6], is only about 22.4%, while the proportion of energy that is carried away from the furnace by gases, dust and water vapor lies in the range from 51 to 70%. For comparison, the percentage of losses of the furnace through conduction, radiation, etc. is approximately 11.6%, melting liquid products carry up to 3% of the energy loss and its loss at the furnace mouth and loss of current are about 2.6 and about 3%, respectively. Such a high proportion of energy that is carried away by gas and dust waste is, according to [6], an inevitable feature of the standard carbothermic process, namely, energy in the form of a technological gas. One reason for this is the use of two tons of reaction gas as a result of the recovery of the first ton of quartzite. Another factor is underutilization of carbon due to the extremely high operating temperatures (>2000°C) of the main reaction of carbothermic reduction. The equilibrium composition of the gas phase in these circumstances corresponds to the yield of one gas product, namely CO, since the oxidation of carbon to CO_2 in this temperature range is thermodynamically impossible. This leads to a doubling of the carbon flow and, accordingly, of the volume of furnace gases, reaching 3500–4000 N m^3 per 1 ton of melted silicon. It is also noted that the amount of energy loss with gases increases with the increasing humidity of the mixture components and the volatiles in them; it reaches 65–68% in the real standard process, which is on average 1.6 times larger than the specific energy consumption that is expended on actually smelting TS. In this regard, in [6] an unambiguous conclusion was made in favor of the development and application of an electric hearth with an enclosed furnace, as well as the utilization of hot gases with their afterburning e.g., for the production of electricity. In [9, 17] the authors proposed to correct the stoichiometrically necessary amount of fixed carbon in the mixture, given its oxidation by water vapor and oxygen adsorbed on coal particles, the proportion of fixed carbon in each of the applied components of the CRA, the size of the fractions and the number of calculated and empirical indicators. According to [9, 17], this gives a reduction in the flow of CRA by 10–15%, an increase in the extraction of silicon by 1.2–2.3%, an increase in the stability of the course of melting, which is the most important indicator in the industrial production of TS, and a decline of nearly 2% in electricity consumption. The above solutions represent the highest achieved level of the technique and technology of the electric-arc carbothermal process for the reduction of silica within its standard form; therefore from [6, 7, 9, 17] we can conclude that all the technical solutions within the standard process are palliative and radical improvement of its performance is impossible. Accordingly, we choose to improve the technology of TS, based on the principles of the formation and supply of a mixture into a furnace with control over the smelting process, and eventually control the process by measuring the magnitude of the operating current in the electric arc. At the first stage we mastered the methodology of the preparation of a mixture as briquettes that include SS from the local Jeroy field with an initial purity of silica of 97.5–98% and 98.5% after processing and performed processes for obtained TS using various CRAs, including those that are a combination of different solid reducing agents with a gaseous one, such as natural methane gas, CH_4.

Table 3 compares the results of a chemical analysis of TS that was first obtained from domestic SS with (a) a different solid CRA, (b) gaseous CRA in the form of methane; when the latter is combined with the solid CRA based on coke that is most available in Uzbekistan, which is obtained by the calcining of Baisun coal without air as described in [4]. It can be seen that the maximum purity of the product can be obtained by complete replacement of solid CRA by methane (Table 3b). However, during smelting gas heat via melting of the mixture and current surges are observed, which may cause process failure.

Despite the fact that the TS that was obtained using a CRA in the form of methane in combination with a solid CRA derived from local coal falls short of the Kr0 type (Table 3c), the result must be considered a success. First, the use this solid CRA is always associated with a number of problems [2, 4], and its benefits are only low cost and availability. Second, a slight decrease in its share in the mixture with compensation for the soot that is produced by burning methane, for example, on the Novoangren TPS, can improve the quality and one can confidently obtain TS of the Kr0 type. In the second stage the range of acceptable ratios between gas and solid CRA was set between 50/50% and 80/20%, within which spontaneous current peaks can be completely eliminated and the optimal ratio for a given solid CRA that is used in a particular process technology may be selected for firing an electric arc furnace due to the lack of operating current surges. A distinctive feature of the technology [18] is relief from the inrush of current caused by rules of melting that provide for periodic feeding of the mixture in a furnace hearth that is fed with deliberately humidified CRA gas directly into the combustion zone of the electric arc.

The developed technology allows one to obtain stable TS based solely on local raw materials with a stable composition of impurities and is acceptable according to this indicator for chemical and metallurgical use with chlorosilane or monosilane schemes for raw polysilicon for the solar industry.

An important advantage of the proposed technology is the reduction of the specific energy consump-

Table 3

a) The results of the chemical analysis of the TS that was obtained from SS with different solid CRSs

Si	Al	Fe	Ca	Ti	Na	K	Mg	Ba	P	V	B	The composition of the briquette and the reducing agent
97.51	0.60	0.66	0.63	0.14	0.30	0.080	0.035	0.026	0.011	0.007	0.0003	SS with a 3% content of wood sawdust, charcoal, and petcoke—45%
97.82	0.66	0.64	0.39	0.20	0.18	0.047	0.015	0.019	0.015	0.007	0.004	SS with a 40% content of technical carbon
97.54	0.74	0.64	0.54	0.16	0.18	0.096	0.025	0.029	0.014	0.006	0.0230	TS charcoal—45%

b) Results of chemical analysis of TS that was obtained from briquetted SS and CRA in the form of gaseous methane

Si	Al	Fe	Ca	Ti	Na	K	Mg	Ba	P	V	B	The composition of the briquette and reducing agent
98.14	0.59	0.58	0.26	0.24	0.089	0.046	0.015	0.0140	0.020	0.0069	0.0006	Briquette is all SS. The reducing agent is CH_4
98.38	0.37	0.60	0.12	0.37	0.058	0.028	0.0087	0.0056	0.027	0.0100	0.0230	
98.10	0.61	0.59	0.24	0.30	0.051	0.025	0.0160	0.0160	0.023	0.0088	0.0230	

c) Typical of characteristics of TS that was obtained from SS with gaseous CRA (up to 80% methane of the total CRA, regulated by the stoichiometric ratio) in combination with a solid reducing agent in the form of coke from Baisun coal

Si	Al	Fe	Ca	Ti	Na	K	Mg	Ba	P	V	B	Composition of a briquette and reducing agent
97.95	0.60	0.60	0.35	0.21	0.12	0.080	0.013	0.017	0.014	0.0058	0.026	The briquette is all SS, the reducing agent is CH_4 (up to 80%) + coke from Baisun coal

tion by 8% or more, which, given the extremely high energy costs of the standard process [6, 7] that range from 10 to 14 MW/h per 1 ton of smelted product, is significant. In addition, it should be noted that the use of the proposed technology does not require significant changes in the technological equipment of the traditional production process. These experimental results and technological developments allow one to regard it as the next stage of development of a fundamentally new process for obtaining TS with a continuous flow of a specially prepared reagent into the combustion zone of an electric arc, including additives of a binder based on alkali liquid-silicon scrap glass, i.e., fine wastes from cutting silicon into wafers and, respectively, from the mechanical grinding and polishing of silicon wafers.

ACKNOWLEDGMENTS

The authors express their gratitude to the Chairman of the State Committee on Geology and Mineral Resources of Uzbekistan I.B. Turamuratov and leading specialist of the State Committee L.A. Panchenkova.

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Translated by L. Speranskaya