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Obtaining homogeneous silicon in the process of aluminothermic reduction of silicon dioxide

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The influence of charge components on emergence of a homogeneous phase of silicon in the process of silicon dioxide reduction by aluminium has been studied. Optimal process parameters affecting the quality of the end product have been identified. These include the ratio of components of the synthetic charge (CaO , SiO_2 , CaF_2), the optimal amount of SiO_2 , the optimal amount of a reducing agent (Al) and the optimal Si /slag ratio. The homogeneous phase of silicon is easily separated from the slag, which contributes to the reduction of waste silicon during further technological operations.

Keywords: silicon, aluminothermic reduction, slag, upgraded metallurgical-grade, solar grade, homogeneous metallic phase.

Introduction

Solar energy is one of the most promising and rapidly growing areas of the global energy generation industry [1-3]. According to the 2017 forecast [3], within the next two decades the global energy industry will undergo revolutionary changes; as a result, the share of solar energy generation may reach around half of the total generation capacity. Rapid growth of the photovoltaic market, whose 90% share is owned by silicon, determines the relevance of the development and improvement of technologies for manufacturing of solar grade silicon (*SoG-Si*) [4-6]. Modern technologies of *SoG-Si* production via the gaseous phase, e.g. the Siemens method, are characterised by multiple cyclical repetition of process stages;

the requirements for accurate control of temperatures, pressures, gas compositions, as well as the explosive nature of the processes, dictate the need for revision of traditional technologies [7-9].

Currently, the process of polysilicon production via monosilane pyrolysis in a fluidized bed reactor (FBR) [10, 11] represents one of the most promising, albeit technologically and instrumentally complex, approaches enabling to reduce the cost of polysilicon by (15-20)% compared to the classical Siemens method [12]. Another approach, which originated in 1980s, is direct purification of metallurgical-grade silicon (*MG-Si*) to produce upgraded metallurgical-grade silicon (*UMG-Si*) meeting the requirements for solar-grade silicon (*SoG-Si*) [12-15]. A number of research centers and companies implemented projects on production of *UMG-Si* [16, 17]. However, these works demonstrated that the quality of initial raw materials in the developed processes must be high and minimum three additional purification stages of metallurgical silicon must be applied in order to obtain satisfactory results.

The development and implementation of novel energy-efficient and technologically simplified processes of silicon production are of special interest. Analysis of literature data reveals that production of silicon via direct recovery of a silicon-containing compound is a promising approach, which has not yet found an application in industry. Metallothermic and carbothermic processes of obtaining silicon by reducing silica are well known, although, the use of organic reducers (petroleum coke, wood chips, etc.) leads to contamination of silicon with hard-to-remove impurities of boron and phosphorous, which presents an obstacle to its use in solar energy [18].

One of the promising ways of producing silicon is the reduction of silicon dioxide using metals according to reaction [19-22]:



where *M* refers to a metallic reducing agent, which may include aluminium, zinc, magnesium, potassium etc.

The reduction process which uses aluminium is known as aluminothermy. One of the characteristics of the aluminothermic method for production of silicon is that it avoids contamination of the target product with boron and phosphorous.

Advantages of the aluminothermic method for silicon recovery from raw quartz material include:

- high speed of the process and low energy consumption per unit of the target product due to the exothermic nature of reactions;
- ability to obtain higher purity of the target product compared to the conventional carbothermic technique;
- high temperature of boiling of aluminium avoids the loss of the reducing agent due to evaporation;
- simplicity and small size of the metallurgical melting furnaces;
- relatively low expenses for the industrial process.

Our earlier works focused on the use of an induction melting furnace for aluminothermic reduction of silicon from small fractional quartzite feedstock, such as ground quartz powder and quartz sand, with further slag refinement to obtain

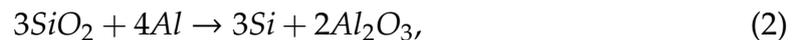
UMG-Si with a low content hard-to-remove impurities of boron and phosphorous [23-26]. Additionally, we conducted studies on the use of induction melting for slag refinement of commercial MG-Si of various grades, obtained via carbothermic reduction. In this process, a small amount of aluminium was required to improve the efficiency of phosphorous removal. It was found that the impurity contents of the best samples of UMG-Si obtained from small fractional quartz feedstock and commercial MG-Si did not differ significantly, showcasing the high efficiency of aluminothermic reduction and slag refinement processes in an induction furnace [27].

In addition to the actual process of aluminothermic silica reduction, separation of the silicon product from a multicomponent slag at the end of the process is an important problem. The aim of this work is to study the influence of charge composition during silicon dioxide reduction by aluminium on the production of a homogeneous phase of silicon in order to facilitate its separation from the slag.

Experimental Part

The aluminothermic process of quartz feedstock reduction was conducted in a Parallel IPT-100-2.4 induction melting furnace. The optimal composition of the starting charge to obtain a homogeneous silicon phase is unknown in the literature. Therefore, we conducted an analysis of melting processes which was devoted to identification of the charge composition and melting sequence resulting in production of the homogeneous silicon phase.

At the first stage, the reaction of silicon dioxide with aluminium, according to formula [22]:



produces silicon and refractory aluminium oxide Al_2O_3 , with the latter absorbed by the slag. It is clear that the amount of slag added into the charge must satisfy a condition that Al_2O_3 is fully dissolved in it. As such, at the end of the process the slag is comprised of three components: Al_2O_3 , CaO and CaF_2 .

During the first series of melting processes, the resulting product poorly separated to higher-density secondary slag and lower-density metallic silicon. As a result, very hard ingots were obtained, which were not readily breakable. Since the slag could not be easily separated from the metal in these samples, silicon could not be obtained for analysis. During further melting processes, the crystalline phase of silicon was obtained in the form of larger islands. Nevertheless, silicon samples obtained in these experiments contained slag inclusions which could not be removed by chemical treatment.

It has been found that the presence of calcium oxide in the slag ensures uniform heating and melting of the charge, bearing a positive influence on the physico-chemical characteristics of the melt both prior to and after the chemical reactions [28]. Due to the heat generated in the reactions, calcium oxide reduces the melt temperature and, therefore, increases the speed of charge smelting. It has been determined that introduction of fluorine-containing fluxing additive of CaF_2 into

the slag, comprising Al_2O_3 , CaO , SiO_2 , results in reduction in viscosity at high basicity ($CaO/SiO_2 = 1.5$ [29]). Additionally, an increase in the amount of fluoride leads to a rise in surface tension of the liquid slag [30]. Altogether, this results in improvement of convectional mixing due to the vertical temperature gradient in the melt. Analysis suggests that to ensure the sufficient level of slag viscosity and surface tension an excess amount of fluorine-containing fluxing additives is introduced. As a result, the slag must ensure efficient absorption of impurities from metallurgical silicon.

Results and Discussion

3.1. Determination of charge composition (CaO , SiO_2 , CaF_2)

To study the peculiarities of aluminothermic reduction of silicon dioxide, melting experiments using various charge compositions were performed. Specifically, the influence of charge composition and process parameters on production of a homogeneous silicon phase was studied. The total amount of charge was selected in such a way, that the melt temperature did not exceed 1450-1600 °C after completion of the exothermic reaction, and aluminium oxide fully dissolved in the slag [31]. This temperature interval is especially favourable, as silicon is produced in molten form and side reactions, such as formation of gaseous silicon monoxide and evaporation of volatile slag components, do not have a negative effect on the process. In principle, higher reaction temperatures may also be used.

Following the oxidation-reduction reactions in the molten phase, slag and silicon are separated from each other: slag descends to the bottom of the crucible, whereas silicon accumulates on the surface. Due to the higher surface tension, slag forms a thin layer between silicon and the wall of the graphite crucible, thereby limiting its contamination with impurities.

3.2. Determination of the slag/aluminium ratio

In a series of experimental melting processes, an optimal range of the slag/aluminium ratio, ensuring homogeneity of the recovered silicon residing on top of the slag, was found to lie between 3.5 and 3.75. This optimal range was determined by visual monitoring of the obtained homogeneous phase of silicon. At a lower slag/aluminium ratio of 3.2, separation of silicon and slag was not observed: instead, small "islands" of silicon were distributed throughout the slag phase. In this case, extraction of the silicon product from the whole charge after cooling was very complicated and required manual work (Figure 1).

3.3. Determination of the amount of SiO_2 in the charge

Another parameter affecting production of a homogeneous phase of the recovered silicon is the excess of SiO_2 which lies in a narrow range. We determined and studied the range of the excess of SiO_2 which influence the occurrence of the homogeneous phase of silicon. The excess of silicon dioxide must not be higher than 20% of the calculated value. For example, at the optimum ratio of slag/aluminium of 3.5 and the excess of SiO_2 being higher than 30% of the calculated value, the recovered silicon does not form a homogeneous phase. However, if the excess of SiO_2 constitutes only 10% of the calculated value, the recovered silicon forms a



Figure 1. Silicon formed as "islands" within the slag phase.



Figure 2. Homogeneous phase of silicon formed on top of the slag.

homogeneous phase and resides on top of the slag. The example of such silicon is seen in Figure 2, which shows complete separation of silicon and slag. In the obtained silicon the trace amount of boron was 1 ppm, whereas the trace amount of phosphorous was ≤ 0.5 ppm, as identified by optical emission spectroscopy.

3.4. Determination of the amount of SiO_2 relative to the reducing agent Al introduced into the melting zone

X-ray diffraction analysis of silicon obtained using the optimum charge composition and the slag/aluminium ratio of 3.5 demonstrated that deviation of the silicon dioxide/aluminium ratio from the stoichiometric one results in a significant change of the calcium silicide content in silicon. In case of an excess of SiO_2 , the content of the silicide phase was 2.65%, whereas in case of a lack of SiO_2 this value rose to 6.23%. This is supported by comparison of the results of X-ray diffractometry measurements in Figure 4, for Sample A produced with the excess

as mentioned earlier in section 1.3. The optimum slag/silicon ratio of $K = 4.7-5.0$ suggests that the amount of slag for the reaction may be obtained using

$$M_s = M_{Si} \times K, \quad (3)$$

The amount of SiO_2 required for the process may be obtained from the stoichiometry of the chemical reaction (1): the amount of SiO_2 must exceed that of aluminium by a factor 1.67.

These calculations were further used in the experiments modelling optimal conditions of obtaining metallurgical grade silicon from oxides with respect to the slag/silicon ratio, whose identification would enable to determine one of the parameters of obtaining a homogeneous phase of recovered silicon on top of the slag.

The slag/silicon ratio is related to the charge composition (SiO_2 , CaO , CaF_2). The amount of SiO_2 varies insignificantly, within 20% of the optimal value, the amount of CaF_2 is a constant, which amounts to 9% of the total mass of the slag. CaO is the only component whose amount varies in a wide range. Following the reaction with aluminium, silicon dioxide is reduced to silicon and leaves the charges, while refractory Al_2O_3 enters the slag composition. As such, as a result of interaction of individual charge components between each other and with Al_2O_3 , formed in the reduction reaction, the slag and silicon are produced.

Conclusion

In this work, aluminothermic reduction of a molten silica-based charge with efficient separation of metallic silicon and slag has been reported. Occurrence of the homogeneous silicon phase is found to depend on both the slag/silicon and oxidizer/reducer ratios. At the slag/silicon ratio of ≥ 4.7 the obtained silicon floats to the surface of the slag forming a homogeneous metallic phase, whereas at the slag/silicon ratio of ≤ 4.7 the silicon spreads across the volume of the slag in the shape of smaller islands. An optimal slag/aluminium ratio is determined to lie in the range (3.5-3.75). As a result, a homogeneous phase of silicon was successfully obtained in the process of aluminothermic reduction of silicon dioxide. The presented results demonstrate viability of the proposed approach for commercial production of metallurgical-grade silicon via this route.

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