CHEMMOTOLOGY AND CHEMICAL TECHNOLOGY

UDC 66.088;661.68; 661.666

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THERMAL INFLUENCE OF MICRODISCHARGE PLASMA ON THE PROCESS OF RECEIVING OF QUARTZ SAND ENCAPSULATED BY PYROCARBON

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Abstract. *The Gas Institute of National Academy of Science of Ukraine developed the facility for pyrocarbon application on the particles of quartz sand through methane pyrolysis in reactor with electrothermal fluidized bed. Thickness of the bed of pure pyrolytic carbon can be controlled within set limits, depending on the temperature, fluid dynamics and duration of the process. The formation of different types of microdischarge plasma takes place at different temperatures. Microdischarge plasma increases the temperature of the individual particles for a very short time, influencing the chemical reaction and the phase transitions passing. Quartz sand encapsulated by pyrocarbon is then used for the carbothermic reduction in order to obtain high-purity silicon.*

Keywords: high-purity silicon; microdischarge plasma; pyrocarbon; pyrolysis.

1. Introduction

High-purity silicon is widely used in solar energy and electronics.

The world's leading laboratories develop new methods to obtain high-purity silicon today. In most cases, technological schemes are based on environmentally hazardous method of its chemical obtaining, using metallurgical silicon as raw material [9].

Receiving of silicon through direct carbothermic reduction of high-purity silicon using reducing agent that contain pure carbon is the potential source of solar marks of silicon [12].

The method of raw material (quartz send encapsulated with pyrocarbon) receiving for further carbotermic reduction developed at the Gas Institute of National Academy of Science of Ukraine applies the electrothermic fluidized bed.

During the passage of current through the fluidized bed particles microdischarges appear, affecting the passage of processes of quartz sand encapsulation by pyrocarbon.

2. Analysis of research and publications

In IHME AS of BSSR [4] the conditions of arc discharge in fluidized bed of graphite particles at different relative expansion layer and temperatures were studied.

Experiments were carried out in column with diameter of 62 mm at constant height of layer equal to 100 mm, using two pairs of horizontal electrodes, one of which is used for heating; another is used to measure voltage of arc ignition.

It was shown that for all analysed layers the voltage of arc decreased almost linearly depending on the temperature of the layer.

Layer heating from 20 to 1000 °C resulted in the decreasing of voltage of the arc ignition from 100-120 to 60 V/cm.

At temperatures higher than 1000 °C, both autoelectronic and electronic emissions impact on the current transfer in the gas. It leads to the increasing of current density in gas discharge.

Discharge switch from spark to arc is also possible.

Due to the fact that argon was applied as the fluid agent, the influence of reaction of fluid agent decompounding was not taken into account.

This can be considered as limitation of this experiment.

In paper [10] the method of research of electric characteristics of fluidized bed, in which current rate that passes fluidized bed is changed in accordance with maximal temperatures, that increase while heat layer admission, is provided.

However, while using this method it is difficult to assess heat losses through the walls of the device and with fluid gas layer due to inaccurate determination of heat transfer coefficients in empirical formulas and complexity of their direct measurement in the experiments, especially in high-temperature fluidized bed.

Experiments previously carried out at the Gas Institute [1, 13] in reactor with a diameter of 100 and 200 mm, with coaxial arrangement of electrodes have shown that layer temperatures of 2000-3000 °C may cause the creation of arc between central electrode and the fluidized bed.

Fluidization was conducted using the mixture of gas and air ($\alpha = 0{,}25$), the field strength was 22-23 V/cm.

It was found that in the Electrothermal Fluidized Bed (EFB) low-temperature gas-discharge plasma appears.

In papers [5-7] the process of obtaining of silicon carbide in EFB was researched.

The authors draw the following conclusion: Electrical discharges between particles establish microplasma field and destroy chemical bonds in reactant's molecules.

At the same time, high-energy activation of reacting components takes place and high temperatures occur in the EFB reactor.

It should be noted that internal heating of quarts sand particles while current passing is principally more effective for heat exchange than its heating with hot steaming gas.

Taking in account all the mentioned above, we can conclude that microdischarge plasma has the significant influence on the chemical reactions passing.

There are the following unsolved problems: determination of the mechanism of the passage of electric current through the particles of EFB, dependence of parameters of quartz sand encapsulation by pyrocarbon on the type of microdischarge.

Objective: Investigation of the thermal influence of microdischarges plasma on the particles of quartz sand during the pyrolysis of methane.

3. Experimental methodology

Studies were carried out in reactor with EFB, developed at the Gas Institute of NASU [2] through pyrolysis of methane.

The reactor includes a cylindrical outer casing, inside which there are two heat insulating layers: external thermal insulation in the form of refractory bricks and internal insulation that is made from carbon black (soot).

In the internal part of heat isolation the reaction chamber with Fluidized Bed (FB) was installed.

Central electrode (anode) is installed in the reaction chamber. Cathode is the graphite body, in the walls of which the copper electrodes are built-in.

Experimental methodology, principle of operation and additional results are described in papers [3, 11].

4. Mechanism of passage of electric current in fluidized bed

If the pair of electrodes in the form of plates will be loaded to the FB of conductive particles and energized, the needle of ammeter that is included in the circuit will oscillate around the average mean.

FB is two-phase system in which particles of solid material are in the suspended state under the influence of flashing gas flow that is uniformly distributed at the facilities section.

The transition from the dense layer to the FB is accompanied by increased hydraulic resistance, while increasing the rate of gas filtration.

Electrical resistance of a dense layer of loose particles is extremely sensitive to the method of slumber, shaking the reaction zone of the layer.

It is the indicator of the unstable contact between particles.

Minimal gas filtration through dense layer leads to disruption of the weakest contacts between particles, redistribution of the ways of electric current passing occurs.

Current goes through the most compacted areas of layer that is filtered, gas velocity increase leads to increase in the number of broken contacts, that is accompanied by increased conductivity.

When fluidization numbers are close to unity, i.e., when the gas velocity significantly exceeds the speed corresponding to the stability limit of a dense layer, the FB represents viscous, low boiling liquid.

The upper limit of the FB is higher than the limit of the dense layer. It leads to the appearing and disappearing of humps that are caused the fact that part of layer raises the gas pimples to the surface.

The appearing and development of gas pimples leads to the fact that the FB becomes inhomogeneous.

In place of gas pimple passing the particles are separated, in other areas there is layers seal.

Local pressure fluctuations associated with the heterogeneity of the FB make individual particles and groups of particles touch each other and the surface of the electrodes.

Along with fixed contacts the sliding contacts also appear. Current pulsates around the mean value, which depends on the voltage between the electrodes and the surface of the electrodes contact with layer.

5. The formation of microdischarge plasma in Electrothermal Fluidized Bed

The passage of electric current in the FB of conductive particles is accompanied with the formation of microspark discharges.

In the relatively low voltage (80-100 V) at the electrode surface and in lower extent in the layer of particles microsparks appear and disappear.

The density of microsparks increases with decreasing of gas velocity.

The main process that causes the spark discharge is the emission of electrons under an electric field influence.

In the FB the distance between the surface of the electrodes and the adjacent particles and between particles varies in a wide range.

When the distance between the particle and the surface of electrode is about micron, field strength is sufficient for the occurrence of spark.

Thus, EFB at low temperatures may cause the occurrence of microdischarge plasma in the form of micro spark discharges in a limited volume of layer due to electron emission process.

At temperatures higher than 1000 °C, both autoelectronic and electronic emissions impact on the current transfer in the gas.

It leads to the increasing of current density in gas discharge.

Microsparks discharges transition in microarcs does not lead to significant voltage drop across the electrodes.

However, layer heating rate increases, and FB electrical resistance decreases due to partial ionization of gas.

While the electrical intensity between electrode and particles is crucial for the occurrence of a spark discharge in a gas, the temperature of electrode, particles and gas, raising of which increases the rate of gas ionization under the influence of thermal and photoelectric emission, is very important for creation and maintaining of arc discharge.

6. Pyrocarbon deposition on the quartz sand particles

Activation effect of quartz sand surface is represented, first of all, in initiation of molecular and radical transformations (1-5) in the gas phase in the boundary of FB in Kassel's scheme [8]:

$$CH_4 \rightarrow CH_2 + H_2$$
$$CH_2 + CH_4 \rightarrow C_2H_6$$
$$C_2H_6 \rightarrow CH_4 + H_2$$
$$CH_4 \rightarrow C_2H_2 + H_2$$
$$C_2H_2 \rightarrow 2C + H_2$$

After the experiments conduction, the appearance of quartz sand particles changed shape and colour.

Depending on the content of pyrocarbon particles have different colours.

Fig. 1 shows image of pure quartz sand before loading of it to the reactor with EFB.

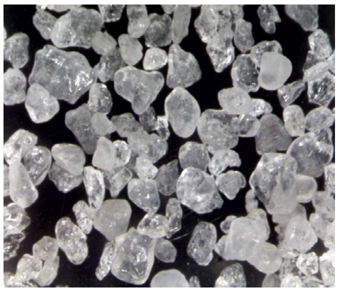
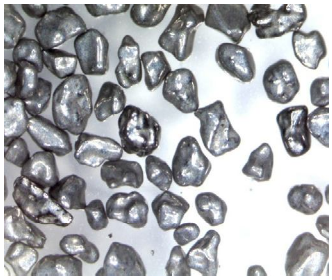


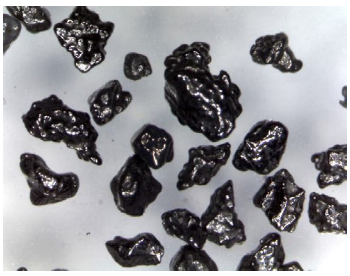
Fig. 1. Pure quartz sand

The particles have crystalline forms, bright colours and do not have sharp angles.

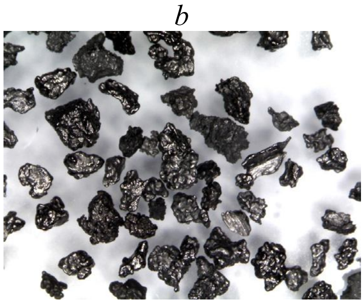
At 30 $\%_{mas}$ of pyrocarbon particles are as follows at Fig. 2, *a*.



a



b



c

Fig. 2. Encapsulated quartz sand:
a – with 30 $\%_{mas}$ pyrocarbon;
b – with 70 $\%_{mas}$ pyrocarbon;
c – with 90 $\%_{mas}$ pyrocarbon

Fig. 2, *b* shows the particle containing 70 % of pyrocarbon.

At 70 $\%_{mas}$ of pyrocarbon particles become darker, luster appears.

Particles are black, have reduced luster compared to the particles with a carbon content of 30 %, have rough shape.

It can be suggested that carbon was in the liquid phase.

We can assume that the temperature of particle was much higher than 900 °C fixed by thermocouple.

Photos of particles of quartz sand with 90 % carbon are shown in Fig. 2, c.

7. Conclusions

The experiments carried out in a reactor with EFB have shown that with increasing of temperature leads to increase of the electrical conductivity of particles fluidized bed.

However, the determination of the temperature of the formation of single particle while the microdischarge creation is impossible with modern methods of research.

In EFB at temperatures less than 1000 °C microplasma discharges exist in the form of microsparks.

At temperatures above 1000 ℃ switch of spark discharge to the arc one takes place.

All the factors mentioned above allow to intensify significantly chemical reactions in the reactor.

In the case of arc discharge, particles have more intense black colour and a larger pyrocarbon content, it indicates that the hydrocarbon perhaps was in the liquid phase.

More detailed description of heat influence of microplasma discharges requires further researches.

The obtained quartz sand encapsulated by pyrocarbon is used for further study of carbothermic reduction, in order to obtain high-purity silicon.

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Received 10 April 2014.

К.В. Сімейко. Тепловий вплив плазми мікророзряду на процес одержання капсульованого піровуглецем кварцового піску

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Розглянуто тепловий вплив плазми мікророзряду на процес капсулювання кварцового піску піровуглецем під час проходження процесу піролізу метану. У результаті проведених дослідів у реакторі з електротермічним псевдозрідженим шаром, в реакційну зону якого подавали метан, зазначено, що під час проходження струму через частинки кварцового піску при використанні метану як зріджувального агенту плазма мікророзряду існує у вигляді іскрових розрядів (до 1000°С), а також у вигляді мікро- і макродуг (більше 1000°С). Після проведення мікроскопічного аналізу одержаного капсульованого піровуглецем кварцового піску встановлено, що при утворенні іскрових розрядів осадження піровуглецю проходить із газової фази, а при утворенні мікро- і макродуг із рідкої.

Ключові слова: високочистий кремній; піровуглець; піроліз; плазма мікророзряду.

К.В. Семейко. Тепловое влияние плазмы микроразряда на процесс получения капсулированного пироуглеродом кварцевого песка

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Рассмотрено тепловое влияние плазмы микророзряда на процесс капсулирования кварцевого песка пироуглеродом во время прохождения процесса пиролиза метана. В результате проведенных опытов в реакторе с элетротермическим псевдоожиженным слоем, в реакционную зону которого подавали метан, отмечено, что при прохождении тока через частицы кварцевого песка при использовании в качестве ожижающего агента метана плазма микроразряда существует в виде искровых разрядов (до 1000° С), а также в виде микро- и макродуг (более 1000°С). После проведения микроскопического анализа полученного капсулированного пироуглеродом кварцевого песка установлено, что при образовании искровых разрядов осаждение пироуглерода проходит из газовой фазы, а при образовании микро- и макродуг с жидкой.

Ключевые слова: высокочистый кремний; пиролиз; пироуглерод;.плазма микроразряда.

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