LOW-SILICON FERROSILICON PRODUCTION FROM IRON ORE MATERIALS IN AN OXYGEN REACTOR

A.V. Pavlov, K.L. Kossyrev, A.E. Semin, A. Korostylev and V.A. Grygorian

Moscow Steel and Alloys Institute, Leninsky pr. 4, Moscow, 119049, Russia. E-mail: kossyrev@mtr.misis.ru

ABSTRACT

A new way of producing low-silicon ferrosilicon from iron-ore materials in a new type of aggregate-oxygen reactor is presented. The oxygen reactor process is based on using the calorific combustibility and reducibility of carbon materials inside the aggregate. The key to the process is successful post-combustion of carbon monoxide above a layer of a solid coke bed.

Initially the possibility of production of grades of ferrosilicon containing 20 to 25% Si (FeSi20-FeSi25) was studied on a laboratory model of the oxygen reactor. Quartz sand and iron ore concentrates (from Russia and India) were used in the laboratory tests. This test work demonstrated that a ferrosilicon grade FeSi15 could be obtained directly from raw iron ore (containing 75.9 % Fe_2O_3 and a maximum of 23.8 % SiO_2) without using rich iron-ore concentrates.

The process was successfully tested on a pilot furnace at Serovsky metallurgical plant. Very promising results and efficiency parameters were achieved. The consumption of materials for 1t of ferrosilicon (15 % Si) production was as follows: 1567 kg raw iron ore, 591 kg of coal (in a composition of ore-coal briquettes), 299 kg of coke (for coke bed formation), and 815 m^3 of oxygen.

1. INTRODUCTION

Traditional ferroalloy technologies for ferrosilicon production require the utilization of high quality raw materials: expensive lumpy quartzite and metallic chips [1]. The size requirements for the blend are necessary to maintain sufficient bed porosity of the raw materials in the submerged arc furnace. In such aggregates the basic reduction processes take place in internal layers of the blend and the free passage of gases through the materials is very important for efficient application of this technology.

It is necessary to note that a shortage of carbon steel chips exists in Russia, due to a sharp reduction in the volume of machine-building during the last decade. This was at least one reason for modifying the market structure in the Russian Federation. The Russian ferroalloy producers preferred to increase the production of high and medium silicon ferrosilicon and practically stopped producing low-silicon grades necessary for industry [2]. Attempts to replace metallic chips by iron-ore pellets in a blend to the submerged arc-furnace were not successful. This was as a result of many technological problems that were experienced, accompanied by an economic problem resulting from the high cost of electric power when reducing iron from the ore.

In the present research, the capability of low-silicon ferrosilicon production using an aggregate mix in a new type of oxygen reactor [3] was studied on laboratory and pilot-plant scales.

According to a developed method, the process is performed in the oxygen reactor (Figure 1). It is represented by a refractory-lined cylinder with the following reaction zones: liquid metal and slag; coke bed zone into which oxygen is introduced through lower lances; zone of post-combustion of carbon monoxide. Carbon is combusted in a flow of oxygen with formation of carbon monoxide. This reaction provides a part of the heat necessary for the reduction processes. Carbon monoxide then reacts with oxygen forming carbon dioxide. This reaction takes place under the arch space of the furnace with the injection of oxygen through the additional top lances above the raw materials inside the furnace. This reaction gives additional heat

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necessary for the reduction and metal formation processes. The raw material is fed to the furnace through the holes in the arch.

The key to the process is post-combustion of carbon monoxide above a bed layer of solid coke. It ensures full use of the calorific combustibility of carbon materials inside an aggregate. Besides that, the presence of a coke bed creates reducing conditions, which allow production of pig-iron and most common ferroalloys. The coke bed protects the metal from re-oxidation by gaseous oxygen.

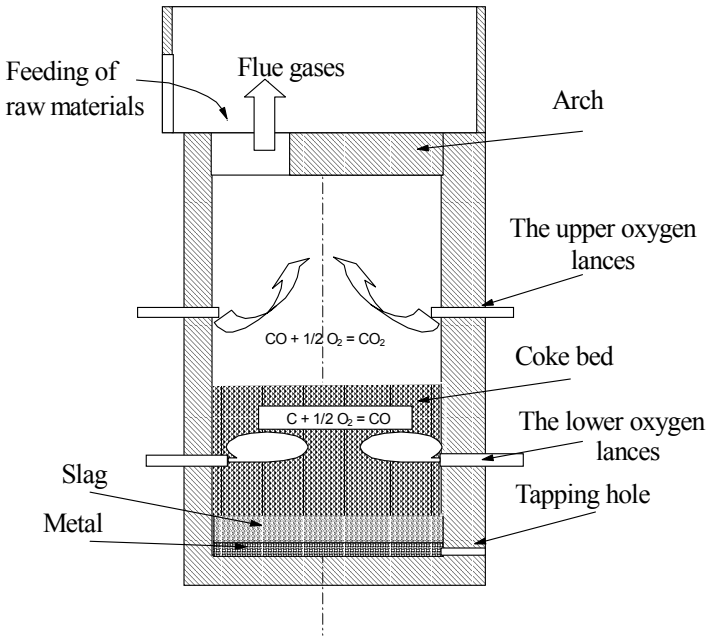


Figure 1. Schematic of the oxygen reactor.

Carbothermic reduction of metal takes place directly in briquettes (or in pellets) lying on the surface of the coke bed. Up to 95 % of the material is reduced on the surface of the coke bed if the composition of the briquette is correct. The reductant in the briquette is coal.

Localization of reduction processes in a thin layer on the surface of the coke bed is the second distinctive feature of the aggregate. This process follows with formation of metal, slag and CO gas. Small amount of un-reacted materials are reduced further by carbon from coke or by CO-gas. However the coke is primarily used for combustion with oxygen to form CO. The metal flows through the coke bed to the bottom of the furnace and is periodically tapped. Using ore as the source of iron plus the use of cheap quartz sand as source of silicon in the ore-coal-sand briquette makes this process more economical.

2. EXPERIMENTAL PROCEDURE

The laboratory set-up of the oxygen reactor (Figure 2) was intended to define the speed and degree of reduction of the various raw materials on a surface and inside the coke bed at operating temperatures.

The installation was constructed based on a resistance furnace with a graphite heater (inside diameter of 85 mm) fed by a 40kW transformer. It consists of the furnace itself (1), a device for adding materials to the furnace at a controlled rate (13), a graphite crucible (4) with a coke bed (6) inside and holes at the bottom and a quartz pipe (9) with a crucible for catching the metal.

The installation was equipped with two thermocouples for the control (10) and regulation (3) of a temperature regime. A photoreceptor was used for registering falling drops of metal and slag. This device allowed evaluation of the stability of the process and registering changes in the continuous recovery of a blend on the coke bed.

The source of heat in the installation was the electrical resistance heater. This was different to the real oxygen reactor, where the heat for the process would be generated by reactions of coke and CO with oxygen. But this difference allows studying of the reduction process taking place on the coke bed "in the pure state" and to avoid the effect of partial oxidation of the reduction products by oxygen. The main heat in the oxygen reactor is formed by the reaction between CO and oxygen, which is generated above the surface of the coke bed. The heat is transferred to materials mainly by radiation.

The installation differs from the real process by virtue of the fact that in the latter continuous tapping of metal and slag is envisaged. It allowed contact of liquid metal and slag with the coke bed to be avoided. As a result it was possible to investigate the reduction process directly on the surface of coke bed. In principle it is possible to conduct experiments keeping the liquid products inside a graphite crucible if the crucible has no holes at the bottom. In this case the composition of the obtained metal and slag mirror the total results of all the reduction stages. But in such a mode it is difficult to evaluate the operability of the process and to interpret the contribution of each reduction stage to the final result correctly.

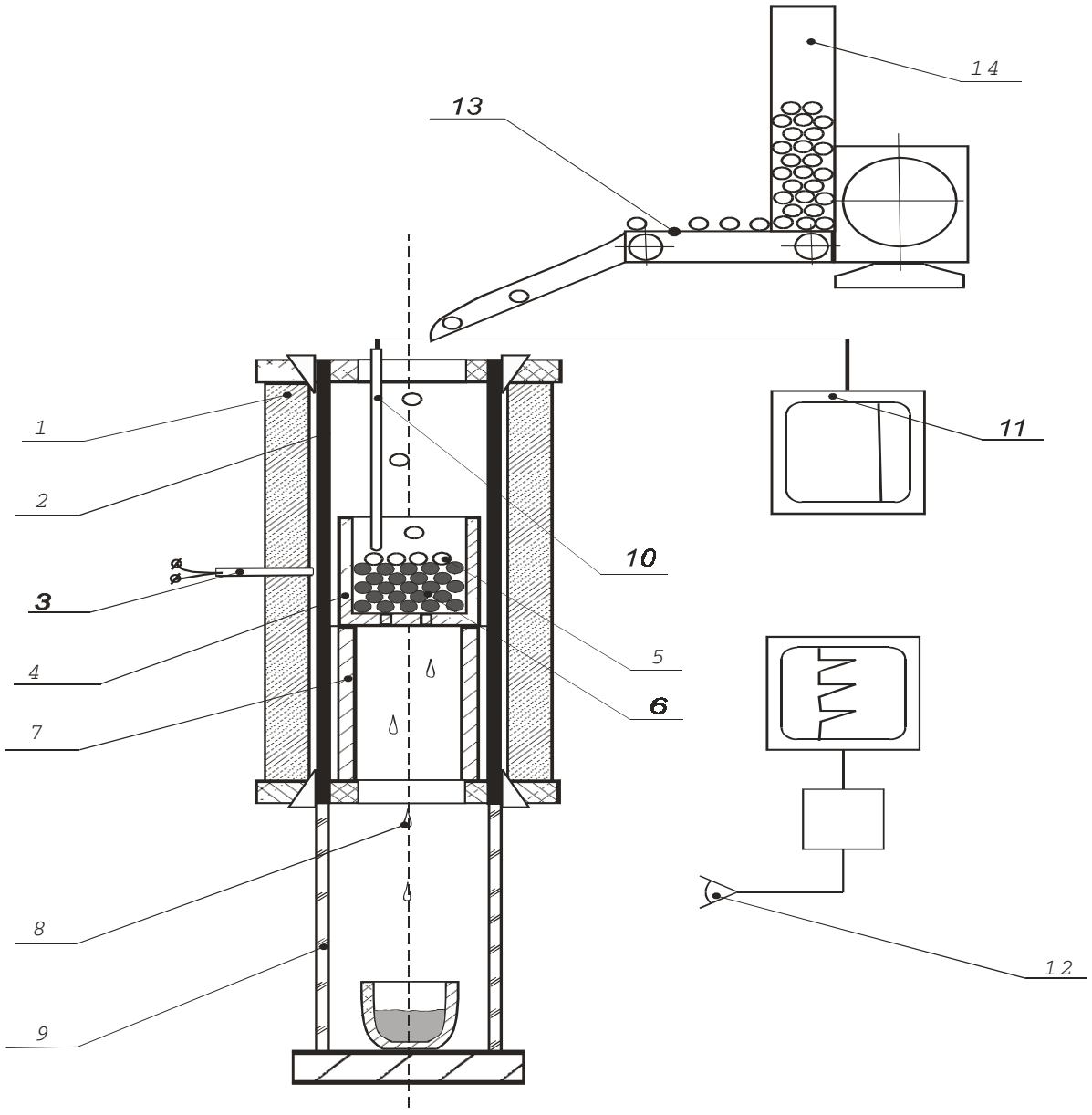


Figure 2. Schematic of a laboratory installation of the oxygen reactor: 1- body of the furnace; 2- graphite heater; 3- regulation thermocouple; 4- graphite crucible; 5- ore-coal pellets; 6- coke bed; 7- graphite support; 8- drops of metal and slag; 9- quartz pipe; 10- controlling thermocouple; 11- measuring equipment; 12- photoreceptor; 13- conveyer; 14- glass bunker.

Before beginning the experiment, the coke bed was designed by mixing pieces of coke and coal in a graphite crucible. The composition of the coke was as follows: carbon - 87%, SiO_2 - 7%, Fe_2O_3 - 0.55%, S - 0.5%, P - 0.065%, moisture - 2%. The coal had the following composition: solid carbon - 70%, SiO_2 - 5%, Fe_2O_3 - 1%, S - 0.4%, P - 0.09%, volatile - 20%, moisture - 10%. Usually the diameter of the pieces in the coke bed was 5-20 mm. The metal reduction from pellets or briquettes proceeds faster than from lumpy ore or agglomerate. This is because the ore and carbon in these materials have an enhanced surface area, so promoting contact for reaction. That was the reason ore-coal pellets were selected for use in the oxygen reactor instead of lumpy ore.

Initially the composition of pellets was decided by results of thermodynamic calculations of metal-slag equilibria. The main criteria for calculations were to obtain the required metal and liquid final slag compositions at the desired process temperature, while simultaneously securing a reasonable content of unreduced oxides. The quantities of carbon material, flux and binder were corrected, based on experimental results with the idea to achieve maximum yield of the alloy and stability of the reduction process, and minimum yield of slag.

Pellets were prepared by the following technique: the ore was crushed down in an impact electromechanical mortar of abrasion resistant manganese steel up to a fraction less than 0.5 mm. Crushed ore was then mixed with required quantities of a reducer and flux (all components had fractions less than 0.5 mm). Then the binder was added to the mixture. All materials were carefully mixed in the mechanical mixer and were pelletized in a plate pelletizer (diameter of a plate - 0.5 m). The diameter of obtained pellets was 7-15 mm. The raw pellets were dried at a temperature of 140^{o}C for 2-3 hours to remove moisture.

The pellets were fed to the installation using a belt conveyor. They were dropped on the surface of the coke bed after an estimated operating temperature was established and stabilized in the reactor. The feed rate was established to create a layer of pellets on the surface of the coke bed of no more than 2 cm thick. Electrical power to the heater was increased to keep the temperature inside the furnace constant.

The ore-coal pellets that fall on the coke bed are heated up. Inside them the reduction reaction progresses and the drops of metal and slag filter through the coke bed. The tapping hole of the graphite crucible allows separation of the stage of oxides recovery in ore-coal pellets on a surface of coke bed from stage of recovery of metal from liquid slag on a demarcation of a slag-coke bed. The commencement of the last stage is unlikely, because it takes place at the bottom of the reactor where the tightest thermal conditions exist. The intensive gasification below a coke bed (as a result of carbothermic reduction) can result in rejection of a blend from the reactor. The speed of melt dropping during the test allows us to control the experiment and to judge the reliability of the selected test mode.

The degree of reduction of the process was indirectly estimated from the chemical composition of the tapped metal, from the composition of slag and metal inside the coke bed after the experiment, from the kinetics of melt dropping from reactor's tapping hole and from increasing or decreasing of the blend level in the reactor.

For example: decrease of a blend level at the intensive melt dropping indicates the lack of reducer in pellets. On the other hand, the increase of a blend level at long-time interruptions or full termination of melt dropping testifies the excess of reducer in pellets.

Excess of carbon in the pellets clog up the surface of the coke bed and hinders the passage of melt drops downward.

The same problem was obtained with the excess of other hard melted phases: formation of slag melted at a very high temperature (which is formed with the excess of flux in a blend) formation of silicon and titanium carbides, etc.

Additional information regarding the process was obtained from the results of material excavation after the test was terminated. When the experiment was stopped, all materials were frozen inside the furnace. The samples of slag and metal were taken from various levels of the coke bed and from the bottom of the furnace.

Slag and metal were carefully separated from each other for determination of chemical composition and degree of metallization.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1 Laboratory Reactor

The following materials were used for investigation of ferrosilicon production in the oxygen reactor: quartz sand (SiO_2 > 97%, Fe_2O_3 - 0.32%, (K_2O+Na_2O+CuO+MgO) < 1.2%, clay component - 0.2-0.5%); Russian iron-ore concentrate (Fe_2O_3 - 99.7%; impurities: SiO_2 < 0.2%, CaO < 0.041%, Al_2O_3 < 0.178%, MnO < 0.009%, P_2O_5 < 0.009%, Cu < 0.003%, Ti < 0.010%, V < 0.005%) or Indian iron ore (Fe_2O_3 - 75.9%, SiO_2 < 23.8%).

Ferrosilicon production with silicon contents up to 20% presented no difficulties and the process was very similar to pig-iron production in an oxygen reactor. We observed some differences to the pig iron process. First of all melt droplets occurred sparsely (with enlarged time interval). Secondly, the slag phase was not found at the bottom of the furnace. The slag melt was always present on the surface of the coke bed. It was in combination with the structure of the frozen coke bed (Figure 3, FeSi20) an indication that the reduction process in oxygen reactor takes place on the surface of the coke bed.

The ferrosilicon (FeSi15) was produced directly from un-enriched iron ore and quartz sand.

The results of visual observations after experiments with different types of ferrosilicon are shown in Figure 4. Each type of ferrosilicon can be produced at specific temperature. In our experiments for the alloys production with concentration of silicon from 20 % to 65 % the temperature should be raised from 1720 to 1850^{o}C. During the production test of alloys with silicon of less than 25 %, the metal passed through the coke bed to the crucible without any problems. The metal composition was exactly the same as it was expected by calculation. The experiments for the production of high silicon ferrosilicon were not successful. In the production of FeSi45, the melt stopped dropping in a very short time. In attempted production of FeSi65, it did not even start. The metal found in the crucible after experiment with FeSi45 had a composition of 25-28 % Si. The samples from coke bed had a silicon concentration of about 40 %. In the production of FeSi65, the concentration of silicon in the metal drops inside the coke bed was less than that estimated by calculation. Practically no metal was observed at the bottom of the furnace.

Figure 3. a) FeSi20

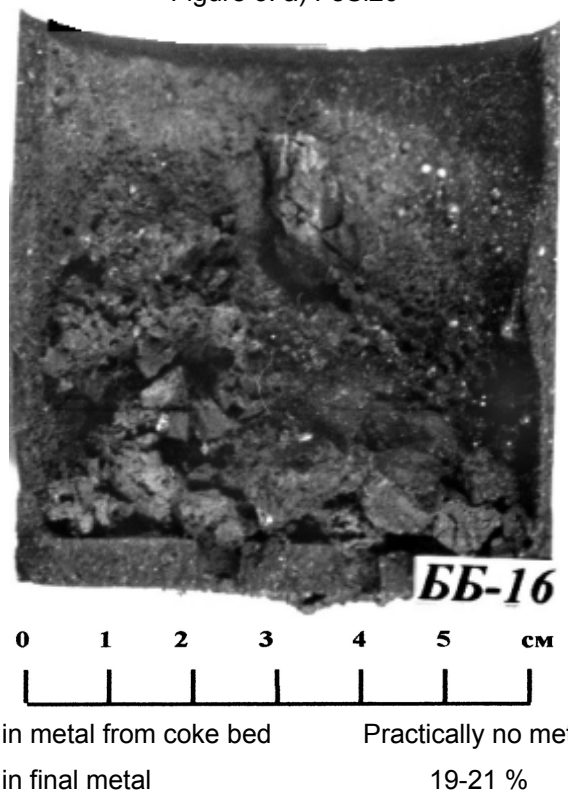


Figure 3. b) FeSi45

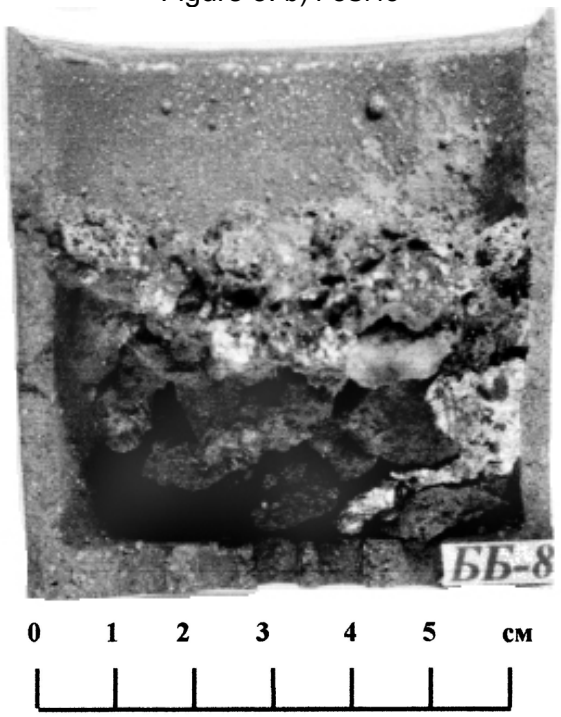
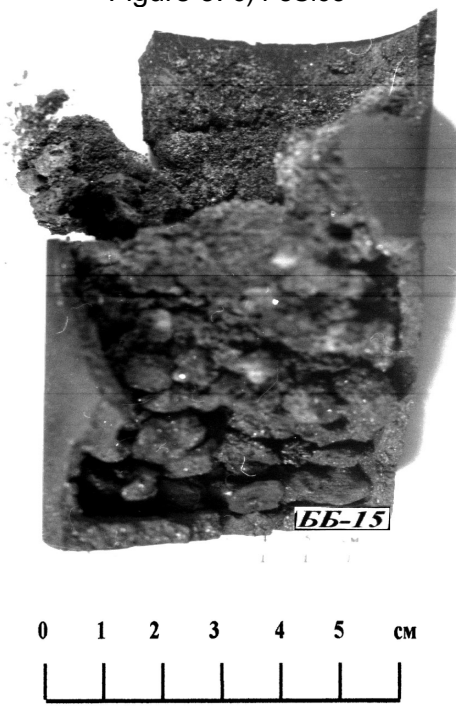


Figure 3. c) FeSi65



Si in metal from coke bed	37-41 %	45-55 %
Si in final metal	25-28 %	No metal

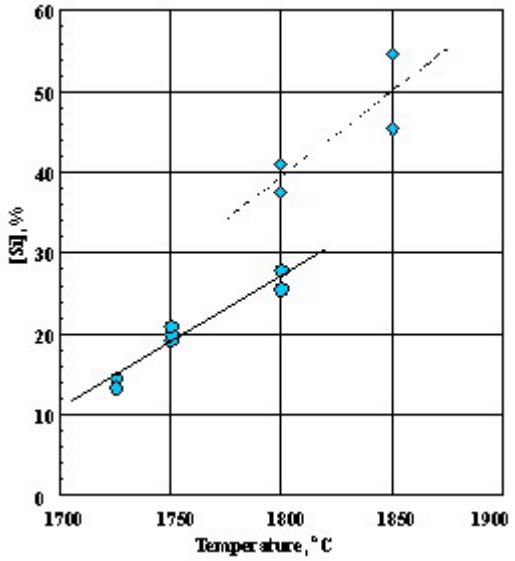


Figure 4. Temperature dependence of silicon concentration in the metal: • - [Si] – final metal; ♦ - [Si] – samples from coke bed.

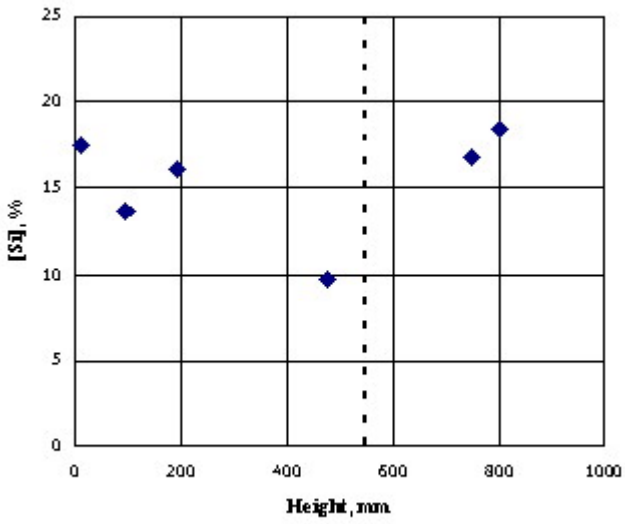


Figure 5. Silicon concentration in the metal samples of the ferrosilicon selected at a different altitude of the "frozen" oxygen reactor: 0 mm - bottom of the reactor; 550 mm - level of the lower lances; 1000 mm - level of a surface of coke bed.

Analysis of the frozen coke bed showed that when attempting high silicon ferroalloys the coke bed was practically destroyed. This effect was accompanied by a degeneration of carbon from coke and coal to green silicon carbide (see Figure 3). According to the Fe-Si-C phase diagram [1] carbon is the primary solid phase for concentrations of silicon up to approximately 23 % at about of 1600°C whereas silicon carbide is the primary solid phase in equilibrium with a liquid at higher concentrations of silicon. This is the main thermodynamic reason for the destruction of the coke bed in the present experiments. In our opinion the

process of coke bed destruction is quite complex. The following reaction takes place during the reduction process directly in the pellets:

$$SiO_2 + C = SiC + CO_{(g)} \quad (1)$$

Besides that SiC can be formed with involving of the gas phase. The reactions could take place inside the coke bed are the following:

$$SiO_2 + C = SiO_{(g)} + CO_{(g)} \quad (2)$$

$$SiO_{(g)} + 2C = SiC + CO_{(g)} \quad (3)$$

3.2 Pilot Plant Reactor

Some experiments for the FeSi15-20 production were also carried out in the pilot furnace at the Serov metallurgical plant. The raw materials used were as follows: quartz sand, mill scale, coke and coal. 8 % of water glass was added to the ore-coal mixture as a binding material and briquettes were prepared from this blend. The briquettes were dried under natural conditions for 10-15 hours.

The wall lining of the pilot reactor was made of magnesite bricks and the roof - of chrome-magnesite. The reactor was equipped with copper water-cooled oxygen lances established at 2 levels: the upper series - 3 lances, the lower series - 2 lances. The installation was equipped with instrumentation permitting us to monitor and to control the oxygen flow rate and to monitor the temperature of the under roof space above the aggregate.

After preheating the aggregate and formation of the coke bed, a predetermined amount of ore-coal briquettes mixed with coke was loaded into the aggregate at a set rate. The coke was added to restore the coke bed, which was burning down near the lower series of lances. The briquette to coke weight ratio was 5,7:1.

The briquettes, falling on the coke bed, were warmed up. The silica and iron oxide in the briquettes were reduced by carbon from coal to form ferrosilicon. The ferroalloy flowed through the coke bed to the bottom of the reactor. The coke bed protected the metal from oxidation. The products of the process were tapped from time to time. The consumption of materials in the pilot aggregate at the production of ferrosilicon alloy with 15 % of silicon was the following in kg/t alloy: iron ore - 1567, coal - 591, coke – 299 kg and oxygen - 815 m^3.

The metal composition corresponded to the standard specification. The process was accompanied by formation of a small amount of liquid slag. The typical chemical composition of slag is presented in Table 1 below:

Table 1. Typical final slag compositions.

SiO_2	Al_2O_3	CaO	MgO	FeO	Fe_2O_3	Fe_{total}
22.7	2.97	36.65	14.32	4.3	1.52	4.4
20.48	3.04	38.81	12.76	4.2	1.35	4.2

After establishing the operational regime, the aggregate feed was stopped and all materials inside the reactor were frozen. Then the oxygen reactor was dismantled to investigate the metal samples from various levels of the furnace. The results of the chemical analysis of some metal samples are presented in Table 2 below:

Table 2. Typical metal compositions from various zones of oxygen reactor.

No. of sample	Si, %	Al, %	P, %	Height, mm
2	18.4	0.091	0.029	800
10	16.8	0.043	0.052	750
13	9.64	0.017	0.038	475
20	16.1	0.044	0.038	195
15	13.7	0.021	0.074	95
5	17.5	0.038	0.038	10

The concentrations of silicon in samples taken from different levels of the reactor are shown also in Figure 5. As can be seen the silicon content in the metal does not depend on the place of sampling. It is an indication of localized reduction on the surface of the coke bed. However, near the area of the lower oxygen lances the silicon content is low. It is probably connected to partial re-oxidation of silicon by oxygen.

Thus, from the present results it is possible to draw a promising conclusion about the possibility of producing low-silicon ferrosilicon in a new aggregate – oxygen reactor. The special benefit of the process is using cheaper raw materials such as quartz sand, crushed coal and mill scale. The composition of ferrosilicon obtained in the oxygen reactor corresponds to standard specifications and previously estimated values.

4. CONCLUSIONS

- The paper describes a new energy and resources saving way for low-silicon ferrosilicon production in a new type aggregate – oxygen reactor.
- The method was investigated in a laboratory condition and successfully tested on the pilot oxygen reactor at Serovsky metallurgical plant.
- Under laboratory conditions with iron ore-coal pellets it produced various grades of ferrosilicon with concentration of silicon up to 23%. Higher concentrations of silicon were difficult to obtain due to reaction of the coke bed with silicon in the metal and formation of silicon carbide.
- The consumption of materials in the pilot aggregate at the production of ferrosilicon alloy with 15% of silicon was the following in kg/t alloy: iron ore - 1567, coal - 591, coke – 299 kg and oxygen - 815 m^3.

5. ACKNOWLEDGMENT

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