INFLUENCE OF COKING PROCESS PARAMETERS ON STRUCTURAL PROPERTIES OF “DIRECSIL” REDUCTANT

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ABSTRACT

Technology of new type of carbon reductant for silicon smelting process was created in Kazakhstan several years ago as a solution to the problem of charcoal shortage. In order to determine the influence of basic coking parameters – temperature and heating speed - on reductant quality a series of high-temperature experiments simulating a real coking process was carried out. Experimental data were further used for assessment of coking parameters influence and optimization of coking process. Results of coke structure investigation show that selected parameters of coking process ensure satisfactory structural characteristics of new reductant important for application in the complex process of silicon recovery in submerged arc furnaces.

1 INTRODUCTION

Numerous researches of complex mechanism of Si recovery in carbothermal smelting of silicon metal confirm the role of gaseous component – silicon monoxide [1-3]. In the final stages of recovery process its concentration in the gas phase may reach 75% [4]. Further disproportionation of SiO gas causes excessive loss of silicon in the form of silica fume carried away with off-gas.

In this situation the ability of carbon reductant to absorb gaseous SiO with further formation of silicon carbide becomes critically important for the process performance. Sorption capacity of reductant in high-temperature conditions of silicon smelting is mainly ensured by high reactivity, developed porosity and large specific surface.

The present work is aimed at investigation of sorption capacity of “Direcsil” reductant for silicon production. A series of high-temperature experiments was carried out to determine the influence of basic coking parameters – heating speed and coking temperature on porosity and specific surface of Direcsil reductant.

Technology of Direcsil production from non-coking high-volatile coal was developed in Abishev Chemical-Metallurgical Institute about ten years ago [5]. Basic application of Direcsil is substitution of charcoal in silicon metal smelting.

Results of the research show that new reductant can successfully compete with charcoal in the complex process of silicon recovery in submerged arc furnaces.

2 METHODS

Initial material for direcsil production is low-ash, high-volatile non-coking coal of Shubarkol deposit (Kazakhstan). Direcsil was created for silicon smelting as a substitute for charcoal which, due to almost complete absence of forests, is very difficult to produce in Kazakhstan. Shubarkol coal contains about 45% of volatile matter and only about 1,5-3% ash. Considering high silica level in coal ash (at least 55%) this material has good prospects in terms of chemical purity – very important parameter for silicon metal process.

Direcsil technology is basically a high-speed thermal-oxidative coking achieved by fast heating of coal by means of combustion of its volatile components.

Modeling of coal processing conditions simulating the real coking process was carried out in Tamman furnace which is a high-temperature resistance furnace with vertical graphite tube. Experiments were made in heat-resistant steel crucible with open access for air.

Initial temperature varied from 600 to 1100°C with 100°C intervals. A batch of raw coal in a steel crucible was placed into the furnace pre-heated to certain temperature. Temperature measurement was continuous throughout the experiment. When the temperature reached given value the crucible was held at this point for 5 minutes with further cooling in a sealed container.

All coke samples were analyzed for technical composition. Results of technical analysis are represented below in “Results” section of the paper.

Results of earlier thermogravimetric analysis of Shubarkol coal [6] show that in the temperature range of 320-540°C occurring physical-chemical transformations are mainly represented by destruction processes with generation of volatile products. Intensity of thermal destruction reactions strongly increases in the mentioned temperature range, accompanied by coal mass loss. The highest speed of mass loss occurs at 420-540°C with active energy absorption and destruction of coal structure. It is known [7] that development of destructive processes depends on amount of input energy in unit of time, i.e. heating speed. The higher the latter the faster the thermal destruction of coal occurs.

High heating speed creates uneven temperature field across the coal particle thus leading to formation of coke frame on the surface. Water steam and gas-vaporr mixture, rising from within the coal body, create excessive internal pressure causing bulging of coke particles. This bulging occurs more actively in oxidizing atmosphere [8].

Thus, based on known data and results of thermogravimetric analysis of Shubarkol coal we can see that the critically important parameter ensuring formation of porous lump material with sufficient mechanical strength is the speed of coal heating within the temperature range of destructive processes. According to [6], in case of Shubarkol coal the minimal heating speed necessary to form porous structure should be at least 10 degrees per minute.

3 RESULTS

Total 6 samples of reductant were obtained at different starting temperatures. Coal samples temperature curves, depending on time and initial temperature, are shown in Figure 1.

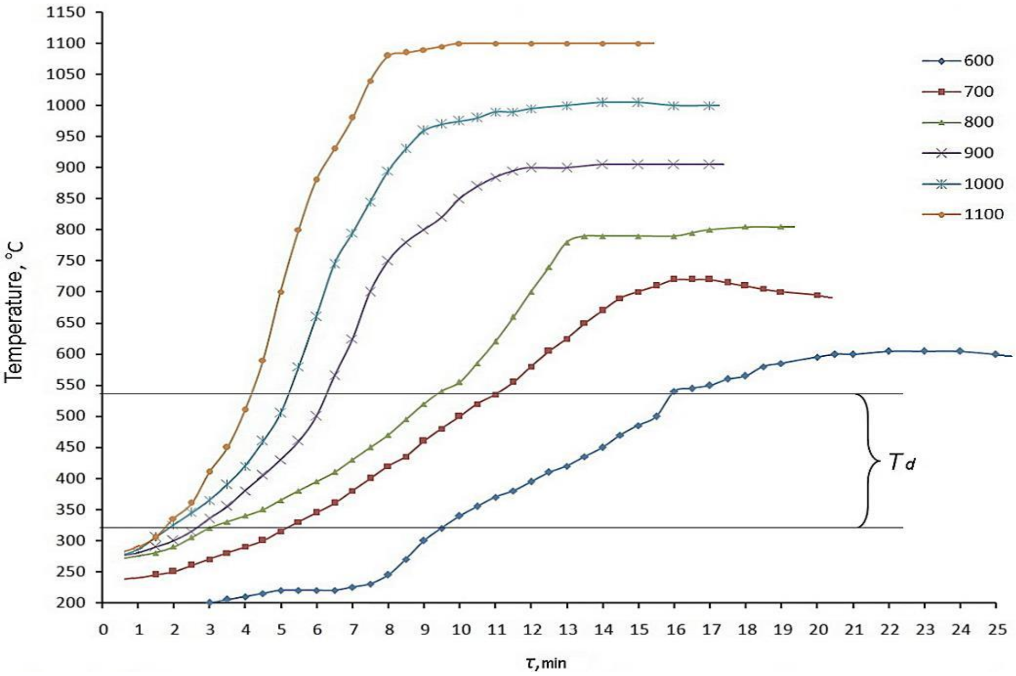

Figure 1: Coal samples temperature variation depending on initial temperature and time

Temperature interval 320-540°C corresponding to destructive reactions temperature range is shown in the diagram as T_d interval.

Data on heating speed, mass loss and technical composition of direcsil samples are shown in Table 1.

Table 1: Results of coal pyrolysis experiments and technical composition of direcsil samples

Temperature, ºC	Heating speed, ºC/min	Mass loss, %	Technical composition, %		
			A^c	V^d	W^r
600	29.41	42.5	3.01	11.02	2.76
700	35.7	47.0	3.23	7.74	3.54
800	45.45	47.8	3.48	3.22	4.17
900	53.57	50.3	3.61	3.04	4.31
1000	65.22	51.0	3.80	2.86	3.16
1100	90.90	49.8	3.95	0.45	3.37

Based on temperature variation data a diagram of heating speed dependence on initial temperature was drawn (Fig. 2).

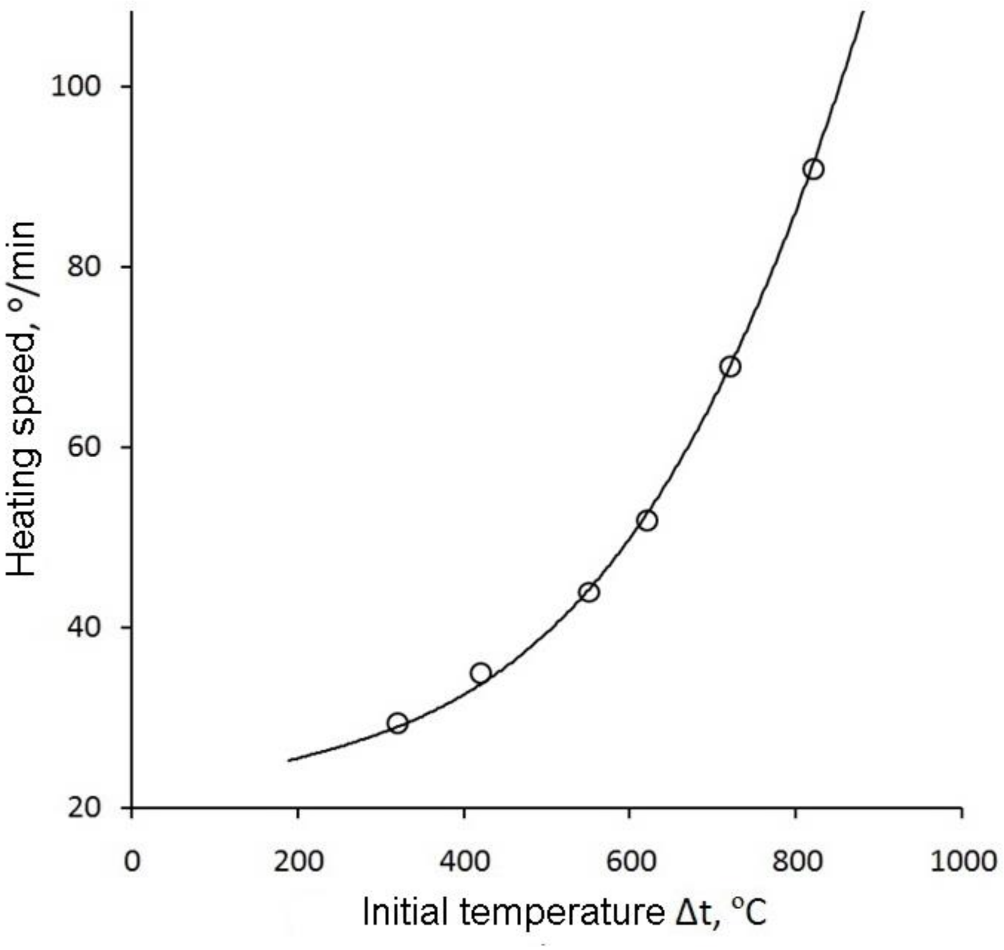

Figure 2: Influence of initial temperature on coal heating speed

As we can see, the speed of coal heating within the temperature range of destructive reactions depends on initial temperature and varies from 29.4 to 90.9 degrees/min, which is sufficient for the formation of highly porous structure of direcsil.

According to technical analysis of direcsil samples, the residual volatile in the coke is strictly proportional to coal mass loss (Fig. 3)

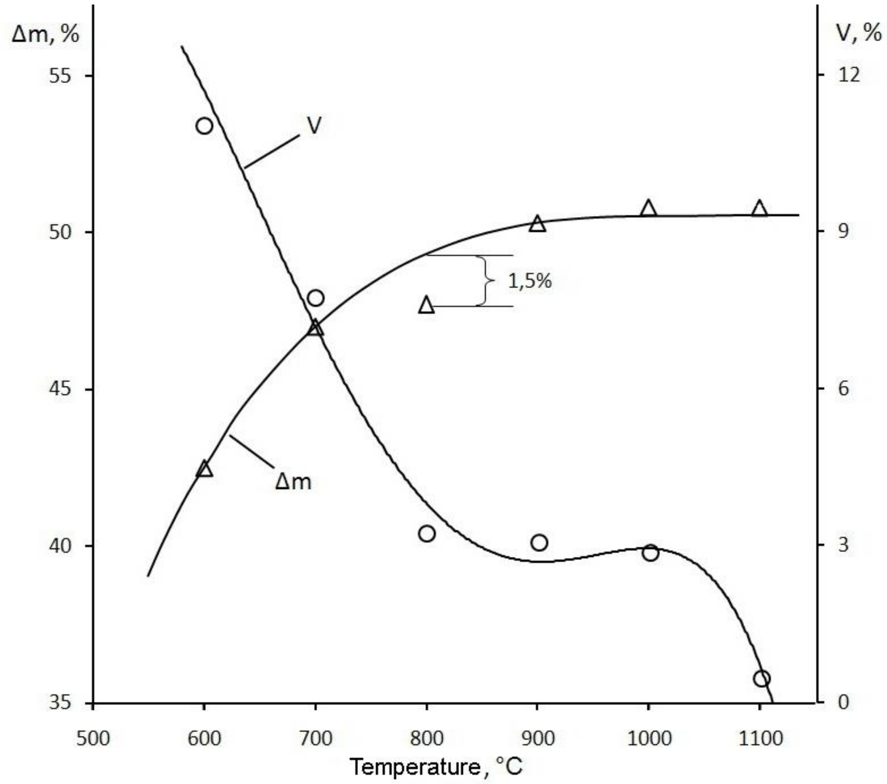

Figure 3: Temperature dependence of mass loss (Δm) and residual volatiles (V)

As seen from the diagram, the most intensive mass loss occurs at lower temperatures of 600-800°C. The fastest decrease in volatiles level also takes place in this area. After 800°C volatiles level stabilizes changing slightly from 3.22 to 2.86% by 1000°C. It is only at 1100°C that volatiles content rapidly drops to 0.45%. This abrupt drop is explained by destruction of coke structure at 950-1000°C accompanied by emission of heavy tars with hydrogen [8].

Samples of obtained reductant were studied using JEOL scanning electron microscope (model JSM-5910). Microstructure of samples at ×200 magnification is shown in Figures 4-9.

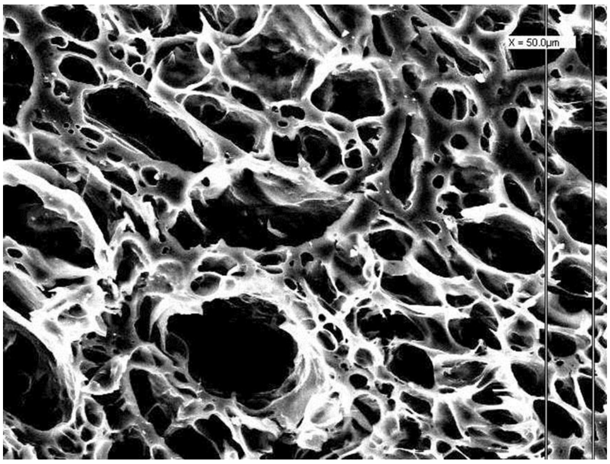

Figure 4: Microstructure of direcsil obtained at 600°C

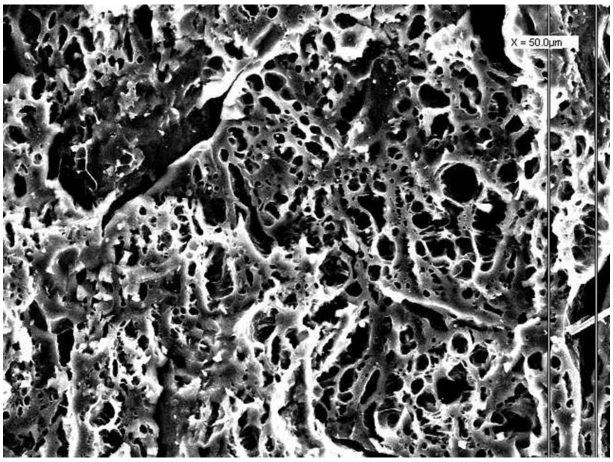

Figure 5: Microstructure of direcsil obtained at 700°C

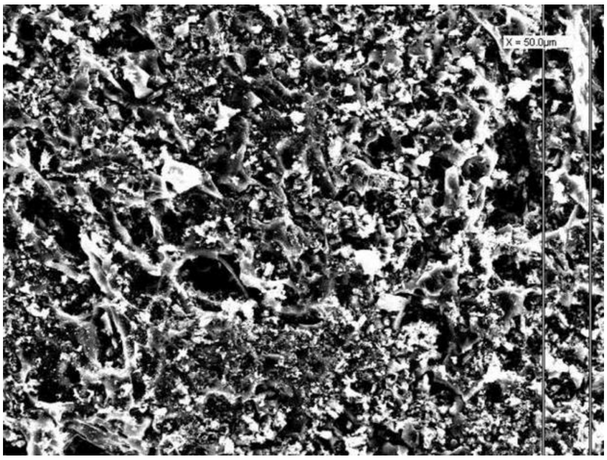

Figure 6: Microstructure of direcsil obtained at 800°C

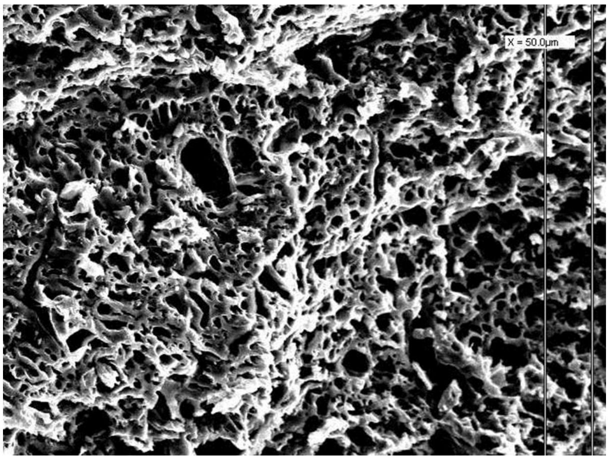

Figure 7: Microstructure of direcsil obtained at 900°C

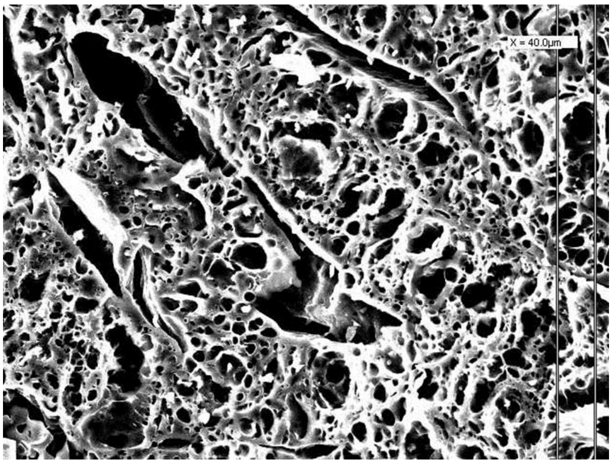

Figure 8: Microstructure of direcsil obtained at 1000°C

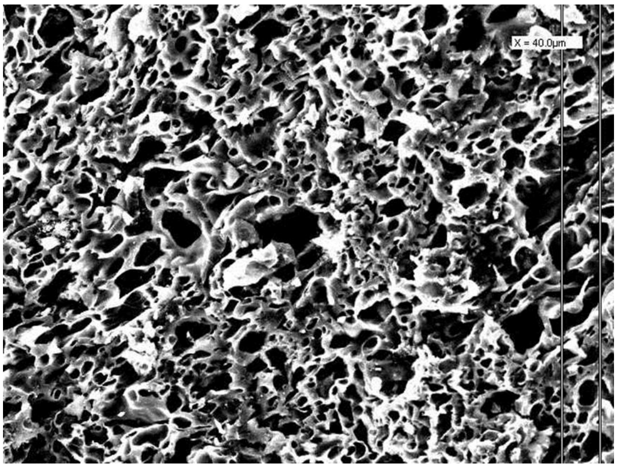

Figure 9: Microstructure of direcsil obtained at 1100°C

Results of microstructure study show that heating speed values reached in experiments were sufficient to form the direcsil structure with well-developed porosity, which evidently depends on coking temperature. We can see that coke structure is formed by pores of varying size – from bigger pores of 150-300 microns to sub-micropores of 0,5-1,0 micron.

Pores have various complex forms, such as interconnecting, one-side open and closed pores divided by interpore partitions. It is known [9] that most efficient type of porous structure ensuring complete and active flow of physical-chemical interaction is a structure formed by interconnecting pores running into one another and joining into integrated macropore or a system of continuous passageways in the coke body.

An important feature of such structure is random orientation and distribution of pores in the material. We can see in the pictures that the structure of direcsil is homogeneous and consists of transition interconnecting pores. Interpore partitions contain smaller pores that serve as connecting canals in the integrated porous system.

4 DISCUSSION

Coking temperature has significant effect on porous structure formation. Direcsil obtained at 600°C has macroporous structure with average pore size about 30.6-54.8 microns and interpore partition thickness around 14 microns (fig. 4).

At relatively low heating temperature substances existing in plastic state have high viscosity. It promotes gradual growth of gas pressure and, thereby, formation of large-pore structure of solid residue [10].

At higher coking temperature (700°C) the amount of gaseous components increases, which, along with higher internal pressure, causes flattening of pores that become more elongated traversing the thermal flow. Compression of coke structure promotes diminution of pores size to 13.5-25.2 microns (Fig. 5).

Further compression of coke structure occurs at 800°C (Fig. 6), although pore size does not change significantly. We can see, however, that pores in the coke body are filled with disperse particles of pyrolytic carbon formed by high-molecular compounds – a product of hydrocarbon pyrolysis.

Pyrolytic carbon, precipitated on the heated surface in the form of spherulites or thin film, has high mechanical strength, resistance to erosion and aggressive media, high electric conductivity and low chemical activity. Therefore, deposition of pyrolytic carbon on the pore surface causes significant passivation of reductant due to dramatic decrease in reaction surface available for chemical interaction with gaseous reagents.

Internal deposition of pyrolytic carbon can be assessed via mass loss value at this temperature. The curve of mass loss (Δm) in Figure 3 shows gradual monotonous growth with stabilization at 900-1100°C. This curve can be described with sufficient adequacy by the following equation:

$$\Delta m = 14{,}496 \ln T - 50{,}229 \qquad (1)$$

with correlation factor $R^2 = 0.96$

However, at 800°C we can see the outlier deviation from general temperature dependence. Numerical value of deviation at this temperature can be determined by comparison of calculated data obtained by equation (1) with results of actual measurement of Δm value. In our case, the deviation value amounts to 1,5% of coke mass. We may safely assume that, in first approximation, this deviation corresponds to the amount of pyrolytic carbon formed by heavy high-molecular compounds as a result of secondary destructive processes.

No significant structural changes are visible with further growth of coking temperature (Figures 7-8). We can see gradual diminution of pore size to 8.38-14.86 microns and interpore partitions thickness to 3.39 microns at 1100°C (Fig. 9). Further development of micropores and interconnecting transition pores is visible while one-end and closed pores are gradually disappearing.

Aside from temperature, successful development of porous structure depends on coal heating speed. Processing of experimental data in coordinates “Heating speed – Average pore size” (Fig. 10) has allowed determining critical (boundary) value of heating speed. Above or below this value we can observe formation of typical structure with predictable physical-and-chemical properties.

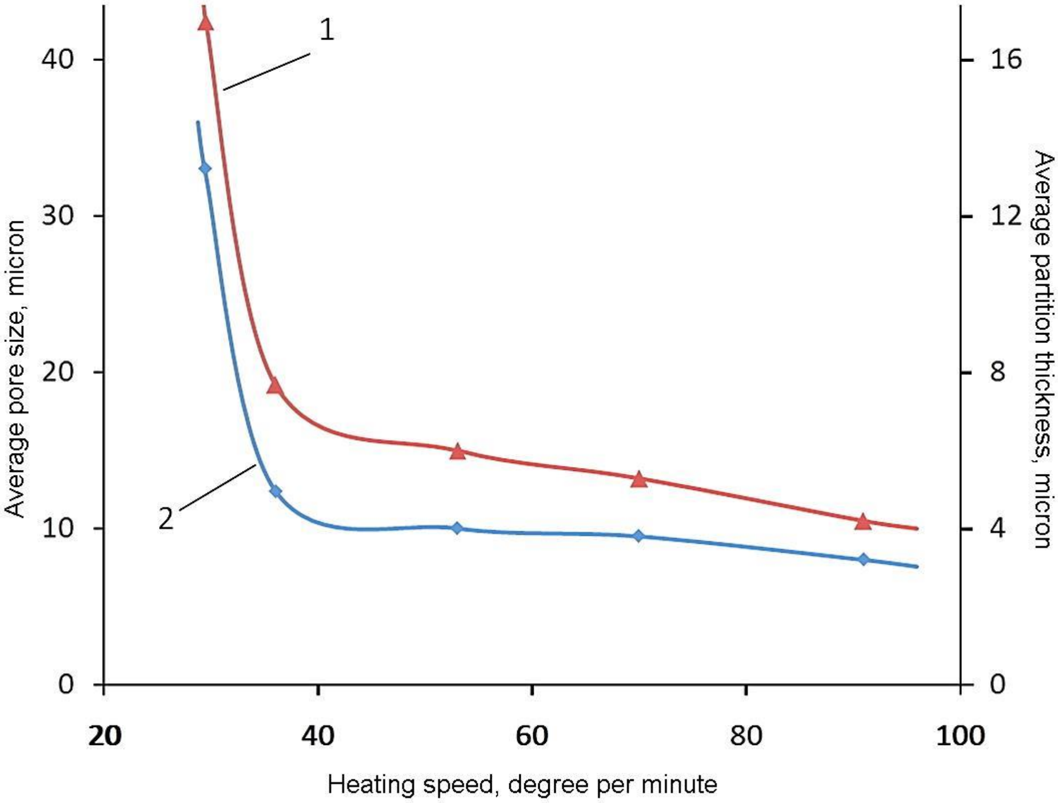

Figure 10: Dependence of pore size (1) and partition thickness (2) on coal heating speed

As we can see from the diagram, the critical heating speed that determines the coke structure is 30-40 °C/min. Below this value average pore size grows rapidly, which causes substantial decrease in internal specific surface of the reductant.

5 CONCLUSIONS

Experimental modeling of thermal-oxidative coking showed that structural characteristics of carbon reductant from Shubarkol coal are closely linked to basic parameters of the process – coking temperature and heating speed. Processing of experimental data has allowed determining the area of optimal process parameters ensuring achievement of necessary physical characteristics of direcsil reductant.

Results of described research can be summarized in the following conclusions:

- thermal destruction of coal is an integral part of coking process responsible for formation of lump carbon material with required mechanical characteristics;
- intensity of destructive processes is directly proportional to the amount of input energy per unit of time, i.e. heating speed;
- both heating speed and coking temperature directly influence the structural characteristics of reductant and therefore can be used as control action instruments to achievef required quality of the final product;
- optimal temperature of the coking process lies above 800°C. Operation in the temperature range of 900-1100°C eliminates formation of pyrolytic carbon inside the coke body thus ensuring high reactive capacity of reductant towards gaseous silicon monoxide;
- minimal heating speed necessary for development of fine-pore structure and formation of large internal surface of reductant is 40 °C/min;
- organization of coking process with strict control of above parameters allows producing high-quality carbon reductant efficient for carbothermal smelting of silicon metal in submerged arc furnaces.

It is necessary to note that, aside from structural properties, the quality of carbon reductant is also determined by its mechanical strength, specific resistance and reactivity. We plan to continue our research work in order to specify the influence of coking parameters on these characteristics.

6 REFERENCES

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