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REACTION RATE OF REDUCTION MATERIALS FOR THE (FERRO)SILICON PROCESS

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ABSTRACT

A method has been developed to measure the influence of a reduction material on the silicon recovery of the (ferro)silicon process. The critical reaction which has been studied, is between carbon and silicon monoxide to silicon carbide. This reaction should be as rapid as possible.

The measurement of reaction rate (reactivity) is carried out in a thermobalance. Particles of reduction materials are placed in a crucible together with a silicon monoxide source. The sample is heated to a given temperature and weighed continuously. The experimental weight loss is an expression of the reaction rate. The conversion to silicon carbide can be calculated.

The measurements have been carried out for a number of cokes for ferrosilicon production. The results seem to conform with furnace experience. The measured reaction rate increased with decreasing particle size. This is in agreement with practical experience and theory.

1. INTRODUCTION

Reduction materials are a main cost in the (ferro)silicon process. The cost of the reduction materials as percentage of the materials and energy cost is about 35% for silicon and 40% for 75% ferrosilicon. The quality of the reduction materials differs and results in different silicon recoveries. Therefore it is important to find a way to characterise the effect of the reduction materials on the process. Then raw materials which give optimal production, low costs and high recovery, can be chosen.

The (ferro)silicon furnace may be divided into two zones: an inner hot zone, and an outer colder region. FIG. 1 shows a schematic picture of this. Silicon is produced in the inner zone. The equilibrium condition for the production of silicon is given by the reaction:

$$SiO(g) + SiC(s) = 2\,Si(l) + CO(g) \quad (1)$$

The temperature for production of silicon is about 2000°C. Then the equilibrium pressure of SiO for reaction (1) at 1 bar is 0.5 bar. To get a high silicon recovery, this silicon monoxide must be recovered in the colder parts of the furnace. The silicon monoxide is recovered by a reaction with the carbon or by condensation. The silicon monoxide which is not recovered, is lost as silica dust. The ability of a carbon material to react with SiO is called the reactivity. If the reactivity is high, much of the carbon reacts to silicon carbide in the outer zone. If the reactivity is low, free carbon may reach the inner zone. Then less silicon and more SiO and CO are produced. Because of the low reactivity in the outer zone, more SiO will condense. Since the condensation supplies heat, there is a limit for the condensation. When this limit is exceeded SiO will leave the furnace.

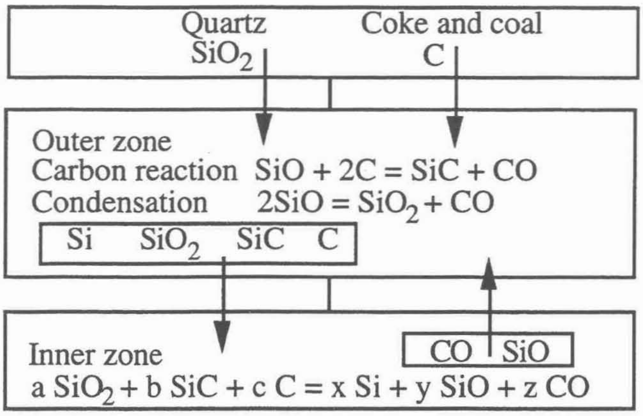

FIG. 1. Schematic picture of the (ferro) silcon process.

If the reactivity is low, the carbon balance in the charge has to be reduced to avoid silicon carbide deposits. Then the silicon recovery will decrease. Further description of the importance of the reaction between SiO and C is given in [1].

There are tests available for describing the reactivity of reduction materials. One is based on the ability of carbon to react with CO_2 to CO. Another method which determines the degree of graphitization (DOG), was developed by Elkem Metals, Niagara Falls. In the DOG method the sample is calcined at 950°C and heat treated at 2000°C. Then the degree of graphitization is measured by wet oxidation or by X-ray diffraction. The assumption is that a low degree of graphitization gives a high reactivity.

In a test which has been in regular use since the early seventies by SINTEF the critical reaction between carbon and silicon monoxide is used as a reactivity criterion [2]. In the SINTEF method a gas mixture of SiO and CO, as produced by reaction between SiO_2 and SiC, is carried by argon through a sample of precalcined and graded material. The composition of the gas mixture before reaching the carbon material is known. The reaction in the sample produces CO, which is determined in the gas going out. With a high reactivity carbon material the CO content stays at a maximum value for a long time and then suddenly drops to a minimum value. With low reactivity the CO drop occurs over an extended time, and some SiO is lost in the gas. The reactivity is reported as the amount of SiO that leaves a sample before the CO content drops below a defined value. High reactivity materials have a low reactivity number.

Elkem wanted to develop a method for measurements of reduction materials that we could use ourselves. Generally a thermobalance was more convenient for Elkem than the apparatus used in the SINTEF test. It was important to use an apparatus where reduction materials of the same size as used at industrial (ferro)silicon furnaces could be investigated.

2. METHOD.

The principle for Elkem's reactivity test is shown in FIG. 2. As in the SINTEF test the SiO source is an agglomerate of SiO_2 and SiC. In the Elkem method the coke sample and the agglomerates are placed in the same container. The reactivity is observed as the weight change in the sample (including agglomerate and crucibles). The reactivity is reported as the percentage of the carbon material which has reacted. A crucible of alumina is used. This crucible is placed inside another crucible made from graphite.

The SiO is produced by the agglomerates according to reaction (2) and transported to the coke particles by diffusion.

$$2SiO_2(s,l) + SiC(s) = 3SiO(g) + CO(g) \tag{2}$$

The carbon in the coke will react with SiO. The aim of the tests is to measure the ability of the coke to react according to reaction (3) in the outer zone of the furnace.

$$SiO(g) + 2C(s) = SiC(s) + CO(g) \tag{3}$$

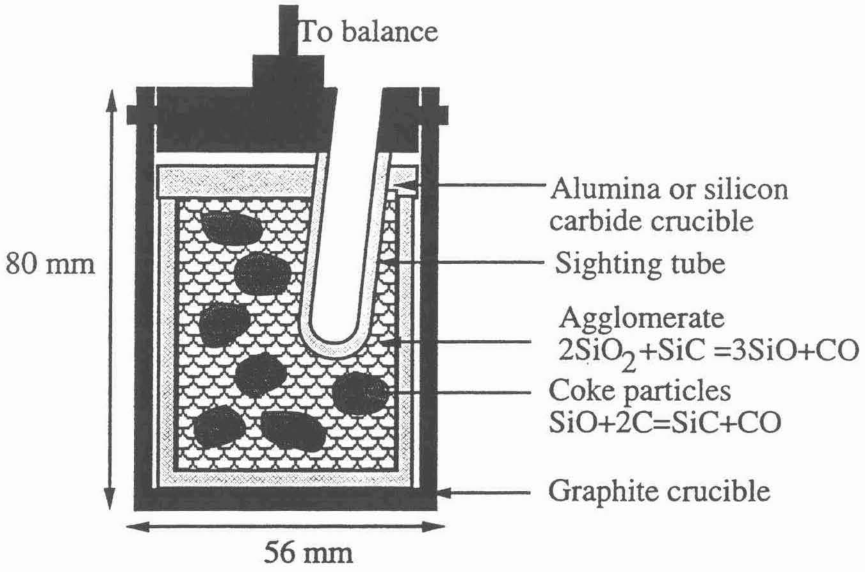

FIG. 2. Principle for testing. Coke, agglomerate and crucibles.

Thermodynamic considerations for the system Si-O-C

The phase rule is given by:

$$P_c + F = k + 1 \quad (4)$$

where P_c is the number of condensed phases, F is the degrees of freedom and k is the number of components. Normally the number of elements will be equal to the number of components in high temperature chemistry. Then the system Si-O-C has $k = 3$. For the agglomerate $P_c = 2$ (SiO_2+SiC), the phase rule gives $F = 2$. For a given temperature and total pressure (here 1 bar) the system is uniquely determined. Equilibrium will be established, and the pressure of SiO and CO can be calculated for different temperatures. FIG. 3 shows the equilibrium pressure of SiO for reaction (2) and (3) together with other reactions in the system Si-O-C at 1 bar. The reactivity tests are normally carried out at 1690°C. Then $pSiO(2) = 0.093$ and $pSiO(3) = 0.0085$. If the agglomerate is heated alone in a closed inert crucible, the reaction (2) will go to the right until equilibrium is established. When the agglomerate is heated, it will react somewhat before equilibrium is reached and a minor weight loss will occur. Then the reaction will stop, and the weight will be constant.

When carbon (coke) is mixed with the agglomerate, $P_c = 3$ (SiO_2,SiC,C) and equation (4) gives $F = 1$. For a given temperature the system is uniquely determined and the pressure is a function of temperature. FIG. 4 shows the equilibrium pressures for the phase combination SiO_2-SiC-C. For temperatures higher than 1514°C the total pressure exceeds 1 bar. Then gas will flow out of the crucible and a permanent deviation from equilibrium is obtained. Then kinetics can be measured by the use of a thermobalance. It was assumed that the agglomerate would produce SiO such that the equilibrium of reaction (2) was sustained when SiO reacted with carbon.

Conversion of coke to silicon carbide

FIG. 5 shows a partially reacted coke particle. Reaction (3) will start at the surface and at pores reaching the surface. A layer of SiC will be formed. For the reaction to continue, SiO has to diffuse to carbon in the coke through pores and cracks in the SiC layer. CO has to diffuse in the opposite direction. The driving force for reaction (3) is the difference between its equilibrium pressure of SiO and the pressure of SiO in the surrounding gas. The rate may be determined by the diffusion or the amount of carbon at the surface. In both cases the reaction rate will increase with decreasing particle size for the same coke. Small particles will give short distance for SiO to diffuse. The surface will also increase and give more carbon available for reaction. If diffusion is rate determining, the reactivity will be proportional to the flow of SiO through the SiC layer. The SiO pressure outside the particle can at most be equal to the equilibrium content of (2). At the reaction zone the SiO pressure corresponds to the equilibrium content of (3).

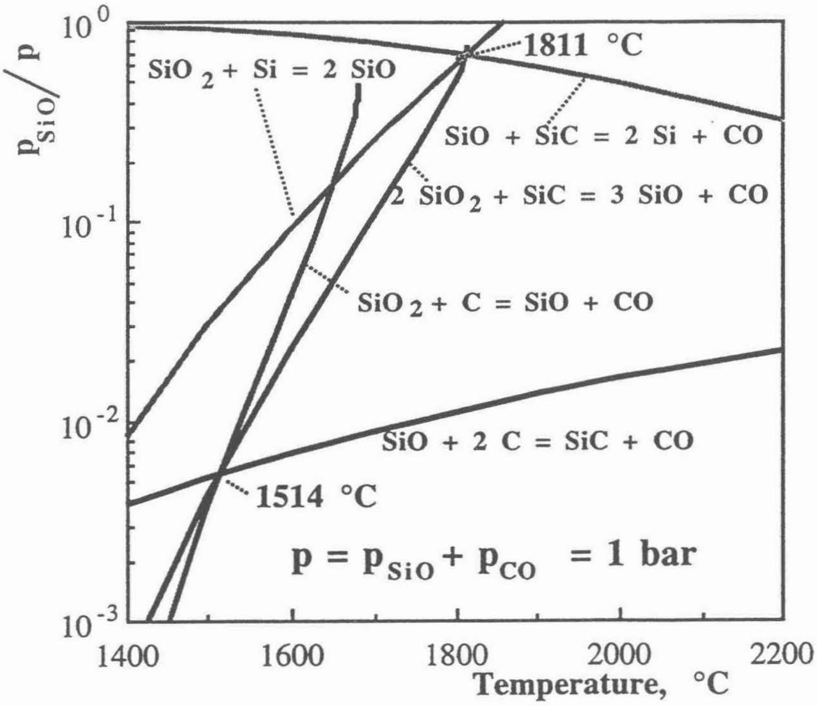

FIG. 3. Equilibrium pressures of SiO as function of temperature for reactions in the system Si-O-C at 1 bar. Data from JANAF Thermochemical Tables [3]

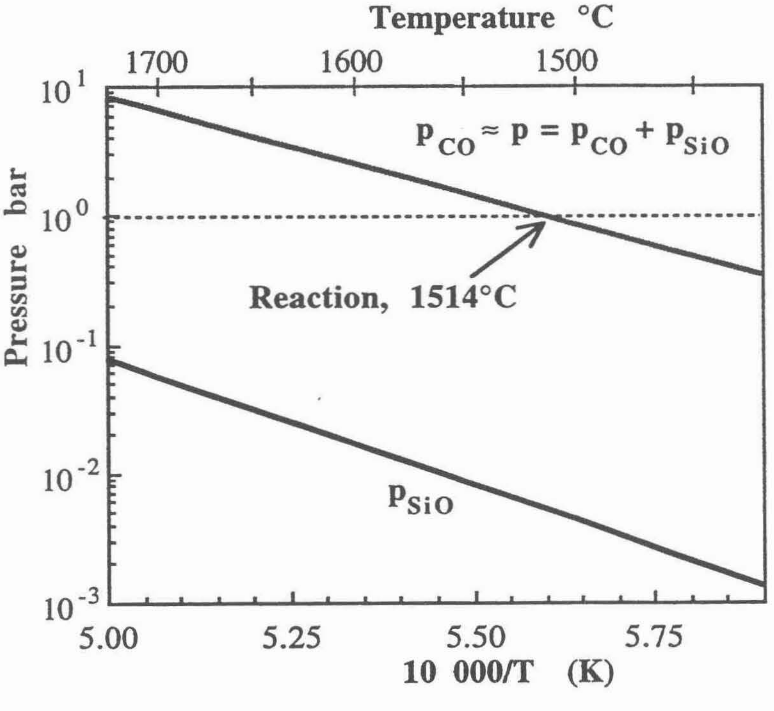

FIG. 4. Equilibrium pressures for the system SiO_2-SiC-C as function of temperature. Data from JANAF Thermochemical Tables [3]

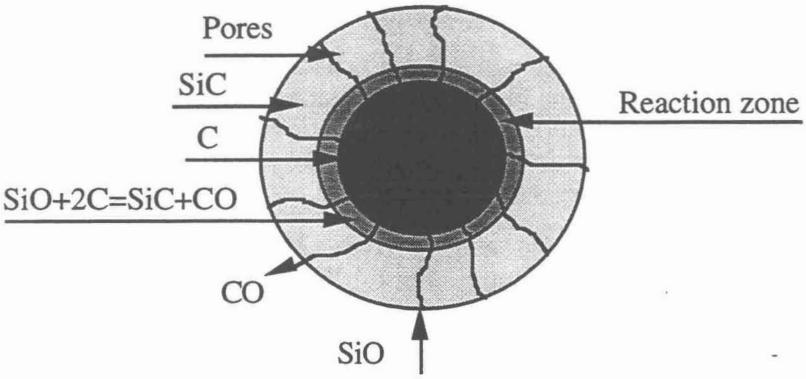

FIG. 5. Partially reacted coke particle.

Calculation of conversion of carbon to silicon carbide

Summation of the reactions 3·(3) + (2) gives

$$2SiO_2\ (s, l) + 6C\ (s) = 2SiC\ (s) + 4CO\ (g) \qquad (5)$$

Reaction (5) gives a weight loss: $4M_{CO}/6 = 18.67$ g per mole carbon reacted. Reaction (3) gives a weight gain: $(M_{SiO}-M_{CO})/2 = 8.04$ g per mole carbon reacted. The gas is diluted when SiO is exchanged with CO in reaction (3). The weight change per mole carbon reacted can be calculated if it is assumed that the effluent gas has the equilibrium composition of reaction (2). Then the overall reaction will be: 3·(3) + (2) + x·(2):

$$2(1+x)\ SiO_2 + 6C = (2-x)\ SiC + (4+x)\ CO + 3x\ SiO \qquad (6)$$

With a total pressure of 1 bar and a given temperature 1690°C: x is 0.1416. Assuming now that the weight loss is caused by reaction (6) the weight loss per unit time expresses the reaction rate. For the amount of carbon reacted, equation (6) gives:

$$\text{Mole C reacted} : \frac{6\cdot\text{weight loss}}{[(4+x)M_{CO} + 3x\ M_{SiO}]} \qquad (7)$$

The amount of carbon that has reacted in percentage of the total amount of carbon in the sample can then be calculated:

$$\%\ \text{C reacted} : \frac{\text{mole C reacted}}{\text{mole C in coke sample}}\cdot 100 \qquad (8)$$

The weight loss in the thermobalance is sufficient to determine the reaction rate and the amount of reacted carbon. The conversion at the end of the test can also be calculated from the weight increase of the coke and from chemical analysis of the coke.

Comparison between the Elkem method and the SINTEF method

The two methods have similar requirements for conformity in particle size, pretreatment of the sample and sample size. Both methods measure the reactivity at only one temperature and one gas composition, and the results apply directly to a strongly idealized process.

In the Elkem test the temperature and gas surrounding each particle should ideally be uniform, and the result for the sample expresses the mean for the particles. The percentage of the carbon reacted is reported as a function of time, and the graph indicates the necessary retention time.

The result is readily interpreted qualitatively in terms of process theory. However, gas flow and limitations in the heat conduction may give deviations from the ideal conditions, and the result gives only a relative measure that is useful for ranking of carbon materials.

The SINTEF method has well-defined conditions in the gas formation and in the reacting carbon materials. The reaction is observed by analysis in the gas leaving the carbon bed, and the result is given as the amount of SiO that has passed before the CO falls below a defined level. The numerical result is not intuitively applicable to the process theory, and it is as the Elkem method useful only for ranking of carbon materials.

The reactivity of a carbon material is strongly influenced by the particle size. In both methods the particle size is limited by the dimensions of the apparatus. For the SINTEF method the particle size is limited to 6.35 mm. In the Elkem method the inner crucible has a diameter of 50 mm. Therefore, all the particle sizes which are actual for use at the (Fe)Si furnace can be tested.

3. EXPERIMENTAL

The measurements are carried out in a thermobalance. It has a water cooled furnace chamber with a heating element of graphite. At the top of the apparatus there is a weighing cell. FIG. 6 shows the furnace chamber. Radiation shields are placed in both ends of the heating element. The temperature is measured with an optical pyrometer. A sighting tube is used for the temperature measurements (see FIG. 2). The heat radiation which is emitted from the target passes through a silica window and is reflected by a mirror to the pyrometer. To correct for the absorption in the window and the mirror, the melting points of copper and nickel were measured. The thermobalance is connected to a rotary pump and an oil diffusion pump.

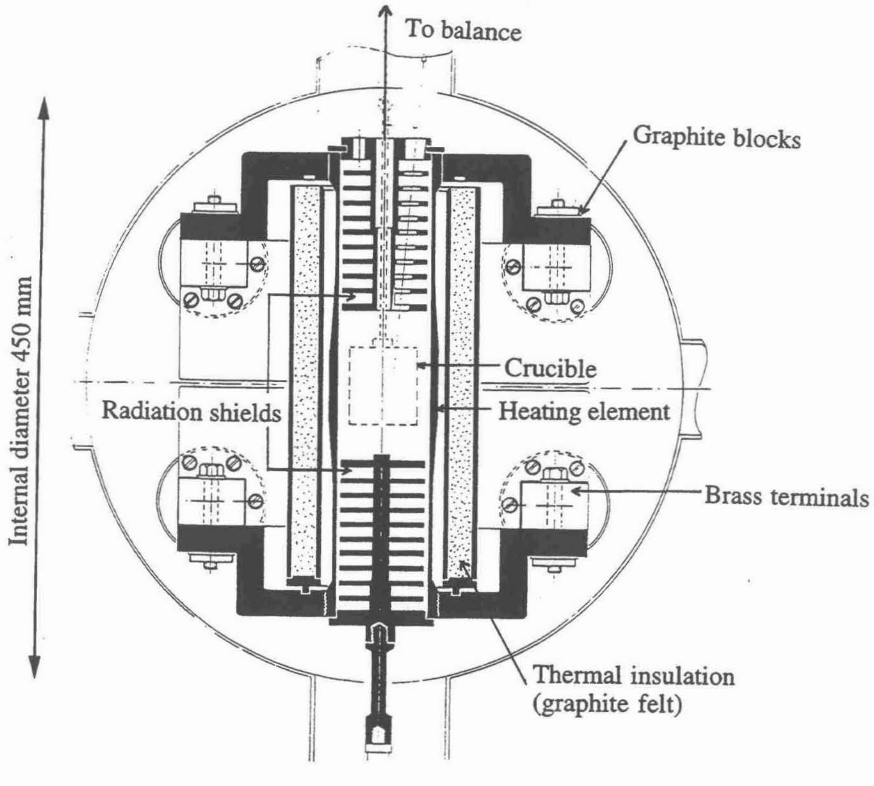

FIG. 6. Furnace chamber.

A standard procedure has been developed for comparison of cokes. Before the test the coke samples were crushed and screened to the fraction 4.0-6.3 mm. Then each sample was heated to 1050°C to remove volatile matter. The agglomerate (the SiO source) was made from pellets consisting of ground quartz and a fine silicon carbide. The pellets were heat treated at 1650°C to sinter and then crushed to the fraction 0.5-1.0 mm.

Before heating the coke, the agglomerate and the crucibles were weighed. The sample was suspended in the balance and the weight set to zero. The apparatus was evacuated and CO was added until the pressure was 1 bar. A valve in the thermobalance lets gas out when the pressure exceeds the atmospheric pressure outside the apparatus. When reaction starts a weight loss will be measured. The weight and temperature are registered in the logging program LabWIEW. Values are normally registered every min. The weight change per minute is calculated and given as Δm/Δt in mg/min.

Short summary of the procedure:

Test temperature:	1690°C
Time at test temperature:	87 min
Amount of fix C:	3.5 g
Amount of agglomerate:	57 g
Particle size	4.0-6.3 mm

4. RESULTS

General behaviour

FIG. 7 shows the temperature and the weight change as function of time. The weight loss starts after about 40 minutes and at a temperature about 1520°C. The test temperature, 1690°C, is reached after 54 minutes. FIG. 8 shows the weight change per minute, Δm/Δt, and the temperature as function of time. The positive values for Δm/Δt in the beginning are due to gas flows in the apparatus and are of no interest regarding the reactivity. A high negative value for Δm/Δt means a rapid reaction. Δm/Δt drops below zero at 40 minutes and continues to decrease until the temperature gets constant.

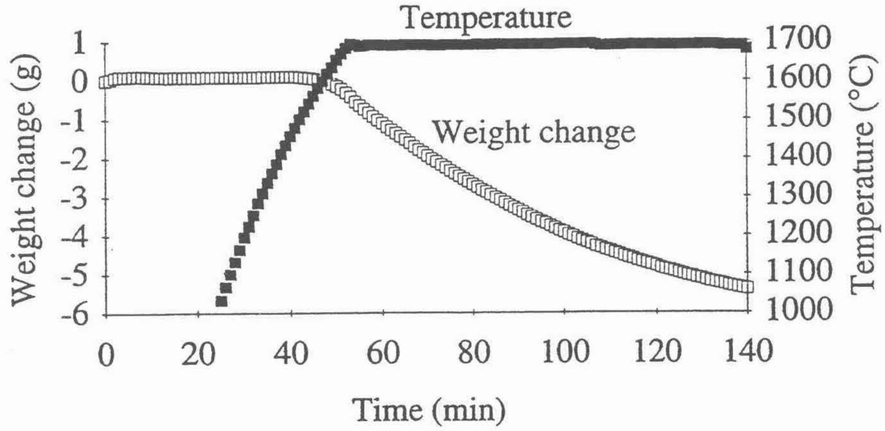

FIG. 7. Temperature and weight change as function of time.

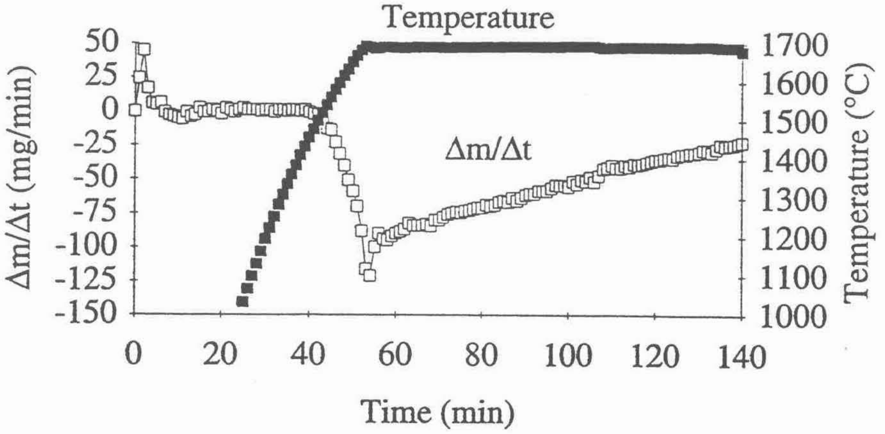

FIG. 8. Weight change per minute Δm/Δt and the temperature as function of time.

After that Δm/Δt gets less negative with time, probably because the reaction rate is limited by diffusion or because there is less carbon available for reaction. For the same amount of carbon in the sample the area between zero and the curve for Δm/Δt will be the same for all samples at complete conversion to silicon carbide. For a coke with a high reactivity Δm/Δt will be strongly negative at the beginning of the reaction. After some time Δm/Δt will move against zero more rapidly for a coke with high reactivity compared to a coke with low reactivity.

Different cokes

Coke A is used as a standard, and is tested regularly to control the stability of the measurements. The coke in FIG. 7 and FIG. 8 was Coke A. For other cokes, normally two parallels are tested. FIG. 9 shows Δm/Δt as a function of time for three samples of Coke A, two samples of Coke D and one of Coke C. FIG. 9 shows that the reactivity decreases in the order: Coke A, Coke D, Coke C. At the end of the test Δm/Δt reaches about the same value for the different cokes. As described in the foregoing chapter, the weight loss decreases with increasing conversion to silicon carbide. The distance of diffusion has increased and there is less carbon available. FIG. 9 also shows curves for the agglomerate heated without coke. In one of the tests the agglomerate was heated in vacuum to 1100°C. Then the effects of the gas flows were avoided. FIG. 10 shows reacted carbon as function of time for some different cokes and for the standard. It is assumed that the reaction of carbon to silicon carbide starts when Δm/Δt gets negative. At this point the amount reacted of carbon is set to zero.

The conversion of carbon to silicon carbide calculated after the test is shown in TABLE 1 for the standard and in TABLE 2 for different cokes. The values are calculated after the test based on the total weight loss in the thermobalance. For the ranging of cokes differences less than 3 are not significant. As can be seen from FIG. 9, FIG. 10 and TABLE 1, the reproducibility of the standard is very good.

TABLE 1. Carbon reacted to silicon carbide for the standard.
The values are calculated after the test based on a) total weight loss in the thermobalance, and b) weight increase for the C/SiC particles.

Coke A parallels	1, 2, 3	Average
a) % (total weight)	82, 80, 81	81
b) % reacted (coke weight)	81, 82, 82	82

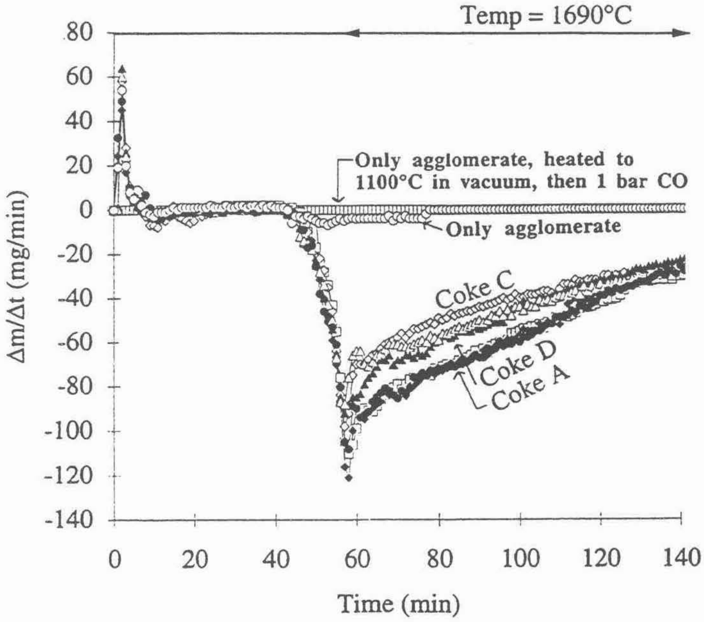

FIG. 9. Δm/Δt as function of time for three cokes and for the agglomerate heated without coke.

TABLE 2. Carbon reacted to silicon carbide for the different cokes.

	% C reacted
Coke E	95
Coke A	81
Coke D	68
Coke B	66
Coke F	66
Coke G	57
Coke C	59

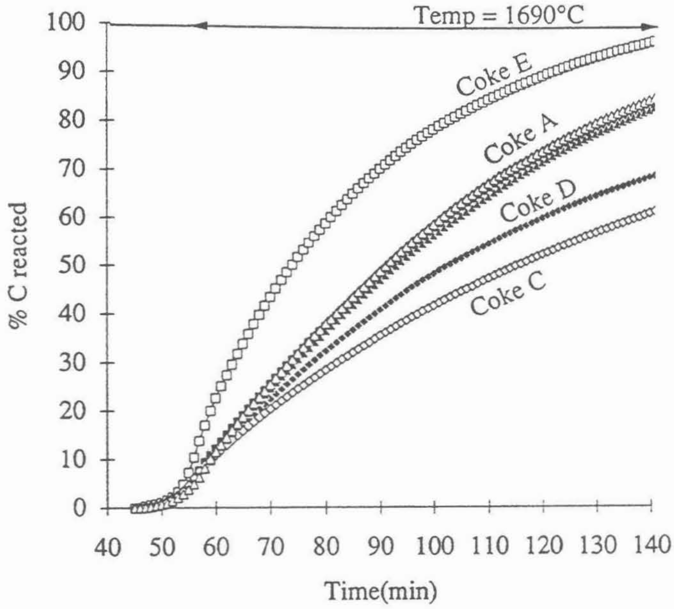

FIG. 10. Carbon reacted to silicon carbide as function of time for the standard and some of the cokes. There are three parallels for the standard.

The effect of particle size

The tests were carried out with a somewhat different procedure. Therefore the results can not be compared directly with the results presented earlier. It was used an agglomerate with sugar as binder in the pellets.

The agglomerate was not preheated. FIG. 11 shows $\Delta m/\Delta t$ as function of time. The reaction temperature was reached after 55 minutes. $\Delta m/\Delta t$ for the agglomerate heated alone is also shown. Volatile matter is driven off the agglomerate corresponding to the peak downwards after about 10 minutes. The second peak is due to reaction between SiO and carbon from the sugar. The reaction rate was highest for the fraction 1-2 mm, considerably lower for 6.7-8.0 mm and somewhat lower for 10-16 mm. This agrees qualitatively with the theory for different particle sizes. (Described at page 4.)

5. DISCUSSION

Tests have been carried out with different amounts of coke and agglomerate. The reactivity decreased with increasing amount of coke and decreasing amount of agglomerate. The reason may be that the equilibrium of (2) was not maintained completely all the time. With a high amount of coke more carbon reacts with SiO. Then the requirement of SiO production to sustain the equilibrium of reaction (2) increases. If there are limits in the SiO production, the pressure of SiO will be lower than the equilibrium content. Then the reactivity will decrease.

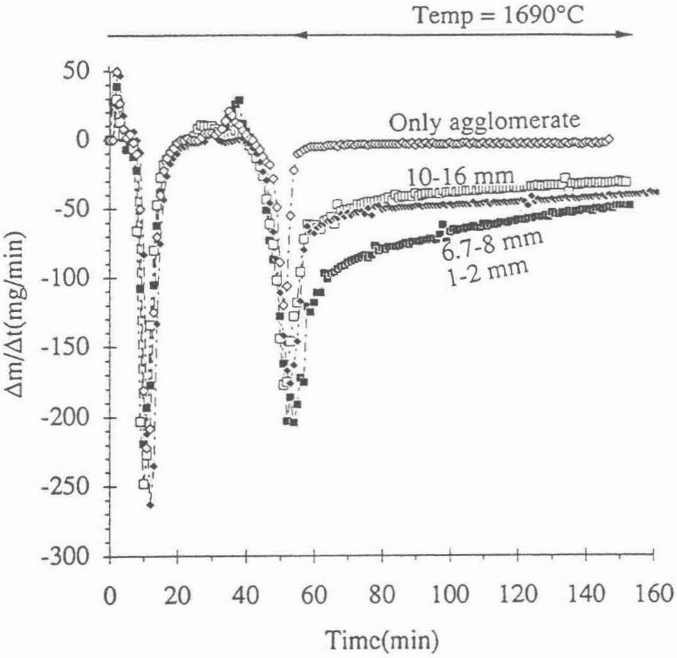

FIG. 11. Δm/Δt as function of time for different grain sizes of Coke A. The test temperature 1690°C was reached after 55 minutes.

Reaction (2) is very heat consuming. For a high amount of coke the increased production of SiO will require increased heat addition. If the thermal conductivity of the agglomerate is low and the necessary heat is not added, the temperature will decrease. As shown in FIG. 3 the pressure of SiO decreases with decreasing temperature for (2). Then the reaction rate for the reaction between SiO and carbon will decrease.

In addition to the weight loss caused by the reaction (6) there may be small weight changes due to reactions with the ash in the coke and because the crucibles are not inert.

Generally, when the reaction between SiO and C is rapid, the reaction rate will decrease as described for a high amount of coke. Therefore the measurements can be used for comparison of cokes but the scale is not linear. At the furnace, the differences between cokes will be larger than measured with the test. The measured ranking of the reactivity of cokes seems to conform with industrial experience.

6. ACKNOWLEDGEMENT

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