Journal of Thermal Analysis, Vol. 36 (1990) 2029-2032

STUDIES OF THE SILICA REDUCTION PROCESS BY CARBON

J. Bialoskórski

INSTITUTE OF MATERIALS SCIENCE, ACADEMY OF MINING AND METALLURGY
30-059 CRACOW, AL. MICKIEWICZA 30, POLAND

The reduction of amorphous silica by carbon black was studied in argon atmosphere by use of MOM Derivatograph C. The apparent kinetic parameters of the process were determined. The possible mechanism of reaction was proposed.

The increasing consumption of SiC sintered products brings about the development of SiC technologies. For this purpose the extended studies of the silica reduction by carbon are carried out. This latter process leads to the production of SiC micropowders of the specific surface higher than 10 m^2/g, without energy consuming grinding operation. As it is commonly known the grain size (and consequently the specific surface) of SiC thus obtained is the function of time and temperature of reaction. The nature of reactants, their specific surface and homogenity are of particular importance [1-6]. The initial reduction is observed at the temperature range 1170-1430°, depending on the factors mentioned above. There is commonly accepted view that above the temperature 1400° the rate of reduction is controlled by the concentration of gaseous SiO, which is formed as a result of SiO_2 dissociation:

$$SiO_2 \rightarrow SiO_g + \tfrac{1}{2} O_2 \qquad (1)$$

or as a result of reduction:

$$SiO_2 + C \rightarrow SiO_g + CO \qquad (2)$$

The process is also strongly influenced by the carbon oxide pressure. The carbon oxide is formed in the reaction (2) or in the following other reactions:

John Wiley & Sons, Limited, Chichester
Kiadó, Budapest

$$½O_2 + C \rightarrow CO \quad (3)$$

$$SiO_g + C \rightarrow Si_g + CO \quad (4)$$

SiC should be formed in the process:

$$Si_g + C \rightarrow SiC \quad (5)$$

The reaction (5) should occur in the particles of carbon component and the SiC particles should therefore preserve their dimensions. This assumption was confirmed by Klinger *et al.* [2] for the reaction between graphite and quartz above 1445°. The process is highly endothermic and accelerated at 1500°. The character of the reaction rate above 1400° is also confirmed by thermodynamic calculations [1, 3]. On the other side, there is no information about the yield of reactions at lower temperatures and the specific surface of the powder product.

The reduction of amorphous silica by carbon black was studied in argon atmosphere. The temperature range, thermal effects and apparent kinetic parameters for SiC micropowders production on larger scale were determined.

Materials and measurements

The ethyl silicate containing 42% SiO_2 (produced by ZA Tarnów) was used as a siliceous component. The carbon black (produced by Carbochem, Gliwice) was also used in the mixture preparation at C/SiO_2 ratio 3, corresponding to the stoichiometry of reaction:

$$SiO_2 + 3C \rightarrow SiC + 2\,CO \quad (6)$$

The mixture was homogenized in ethanol by means of ultrasonic disintegrator and propeller mixer and subsequently hydrolized in the presence of 10% hydrochloric acid. The suspension was dried at 120-150° for 70-100 to produce the dehydration, shrinkage and crushing of gel-like siliceous component in the mix. The 50-60 mg samples were subjected to the DTA measurements by means of MOM Derivatograph C. The apparent kinetic parameters were determined using the program basing on the Kissinger method. The samples were heated in argon atmosphere at the rates

10 deg/min in the range 20-1000° and at 5 deg/min in the range 1000-1500°. At 1500° the samples were heated for 60 min (isothermal heating).

Results

The typical experimental curves are plotted in Fig 1/a. At 20-300° the weight loss corresponding to the SiO_2-gel dehydration is observed and at 1140-1550° the other weight loss due to the CO evolution, according to the Eq. (6). The CO content results from stoichiometry of reaction (6) and the deviation is ±0.5%. The process is completed at 1550°. From the DTG data the following apparent kinetic parameters of the process were calculated: the reaction (process order 1.4, activation energy 376 kJ/mol and the factor in the Arrhenius equation $A = 10.7$.

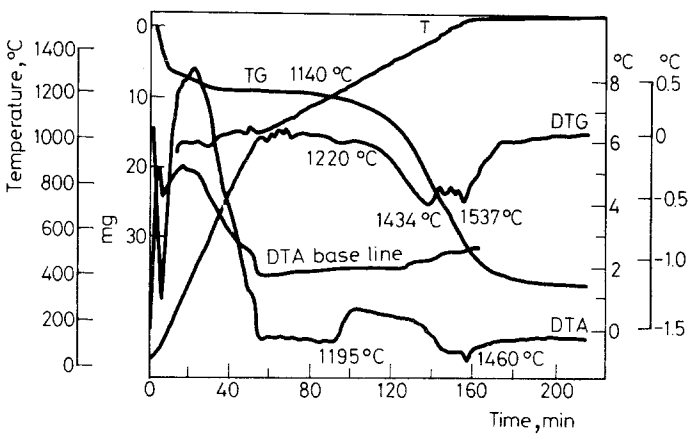

Fig. 1a T, TG, DTG, DTA curves and DTA base line for the reduction of silica by carbon black

The calculated activation energy value is lower from that for the reaction quartz-graphite [1]. This difference of 110 kJ/mol can be explained by a 300° higher temperature range of the process. The great discrepancy relates to the reaction order, which for the quartz-graphite reaction is 1/3 [1]. This latter process is controlled by the reaction (4) occurring on the surfaces of graphite particles [1] while the value 1.4 corresponds to the more complex process including several reactions (1-5), controlled by the surfaces of two reactants and the concentrations in the gaseous phase containing CO and probably SiO. The occurrence of exothermic peak at 1195-1460° (Fig. 1a),

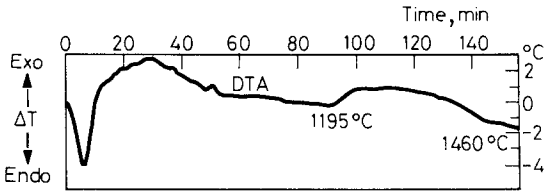

Fig. 1b DTA curve modified by subtraction of base line for the reduction of silica by carbon black (scale changed)

which is not consistent with the commonly accepted endothermic character of the process is difficult to explain. To eliminate the apparatus factor the basic zero curve was subtracted. The effect is shown in Fig. 1b. Only the reaction (3) and (5) are exothermic but the calculation for the reaction (1), (4) indicate that the process (6) is endothermic. This disaccordance may be explained by utilization of the amorphous components but the further investigations are necessary. The reduction of silica by carbon must be studied by mass spectrometry to evaluate the gaseous products. The mechanism of the process would be thus elucidated. This problem is important because the SiC powders produced on a laboratory scale show highly developed surface from a few to tens m^2/g [6].

References

1 N. Klinger *et al.*, J. Amer. Ceram. Soc., 49 (1966) (7) 369.
2 W. L. Li *et al.*, Ceramic Powders, ed. P. Vincenzini, 1983, p. 403.
3 G. C. Wei *et al.*, Ceram. Bull. 63 (1984) (8) 1054.
4 G. C. Wei, J. Amer. Ceram. Soc., C-111, July 1983.
5 L. A. Harris *et al.*, ibid., C-121, June 1984.
6 R. Pampuch *et al.*, Patent P-273394 (1988).

Zusammenfassung — Unter Verwendung eines MOM Derivatograph C wurde in Argonatmosphäre die Reduktion von Siliziumdioxid mit Ruß untersucht. Es wurden die scheinbaren kinetischen Größen des Prozesses bestimmt und ein möglicher Reaktionsmechanismus vorgeschlagen.