

COMPARISON OF MASS LOSS RATE IN REACTION OF SILICA WITH CARBON FROM DIFFERENT INVESTIGATION RESULTS

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In the process of carbothermic reaction of $\text{SiO}_2 + m\text{C}$, key reactions appear on the surfaces of both SiO_2 and C grains. However, the values of these surfaces are not known. Assuming the simplest case, quartzite and carbon grains are spheres, total surfaces of reaction were calculated for grains of carbon and quartzite respectively. This enabled to determine the rate of weight loss referred to the unit area of C and SiO_2 .

Key words: silica, carbon, mixture, carbothermal, reduction

INTRODUCTION

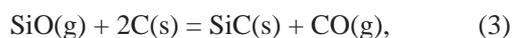
Above the temperature of about 1 800 K thermodynamic conditions are favorable to the formation of SiC according to reaction [1]:



Among many possible, reference here is made to several exemplary results of studies of kinetic reaction $\text{SiO}_2 + m\text{C}$ and SiC formation. These tests vary in a number of parameters and factors. Some of them are summarized in Table 1. The results of kinetic studies conducted in laboratory conditions contain many ambiguities and inconsistencies. This generates a number of questions, e.g. how to compare the obtained results.

In the studies of silica – graphite mixture by Shimoo et al. [2] in argon atmosphere, the product of the reduction was SiC and SiO. In the early stage of reduction of SiO_2 by graphite it can be described by the equation reaction rate for interfacial reaction control. It is believed that the rate-determining step is a chemical process on the surface of graphite particles. When the reaction proceeds further and a continuous SiC layer around the graphite particles is created, the rate of reduction reflects the parabolic rate equation. Then the reduction of SiO_2 is controlled by diffusion of carbon in SiC.

According to Agarwal and U. Pal [3] at the temperature above 1 773 K key reactions in the carbothermic reduction process are:



It is assumed that reaction (3) is very fast in comparison with reactions (2) and (4). According to authors

Table 1 Comparison of chosen parameters of some investigations

Investigation/ Parameter	[2]	[3]	[4]	[5]	Present study
ϕ particle SiO_2 / μm	143	10	40	10	200
ϕ particle C / μm	7,5	20	1	10	50
Type of Carbon	Graphite	Carbon black	Carbon black	Graphite	Graphite
Mass of sample / g	5	1,2	0,175	2,796 *1)	0,10
Form of sample	Pres- sed	Pres- sed	Pow- der	Pres- sed	Pow- der
C/ SiO_2	1, 2, 3, 4, 5	3, 5, 10	1	45	3

*1) mass estimated in the article

[3], the reaction rate is controlled by the combination of reduction reaction of silica and Boudouard reaction, i.e. the reaction expressed by formulas (2) and (4).

In studies by Wodopianow et al. [6] the reaction between separated substrates was the fastest in CO atmosphere, slower in argon and the slowest in vacuum. On the other hand, Agarwal and Pal studies [3] show the opposite; namely, the authors reported a higher rate in Ar atmosphere than in CO.

The reaction, particularly in its first stage, is strongly correlated with the evolution of CO [4] and [5].

In case of proportion C/ $\text{SiO}_2 = 3$ a certain amount of SiO leaves a lump [3]. According to the authors [3], such emission is also caused by the application of loose, not compacted powder; whereas Wotzak and Biernacki [4], studying the kinetics of the non - compacted mixture of $\text{SiO}_2 + \text{C}$ powders at a ratio C/ $\text{SiO}_2 = 1$, don't mention any released SiO in exhaust gas. Moreover, at the top of the sample the inert diffusion layer (SiO_2) was placed. For samples with such a layer, escaping CO could have favorable conditions to react with SiO_2 layer by reaction (2), but authors do not mention this.

Examples of thermodynamic calculations of equilibrium composition as a function of temperature in Si – O – C system, for mixtures with initial molar proportion C/SiO₂ equal: 1,74 [1], 2 [7] 3 [3], and 45 – calculated in this paper – don't reveal CO₂. Also in laboratory kinetic studies [2–4] the presence of CO₂ gas in discharged gases is not mentioned. On the other hand, experimental results of Sahajwalla et al. [5] reveal CO₂ emission.

PRELIMINARY STUDIES

Our own preliminary studies were performed with thermobalance “Thermogravimat” 4304 series Sartorius redesigned for the tests. The tests were done in a gas stream introduced from the top of the reactor tube ($\Phi_{in} = 27$ mm). The Al₂O₃ crucible (dimensions $\Phi_{out} = 9,7$, $\Phi_{in} = 7,1$, $h = 14$ mm) with the sample, placed in the reactor, was suspended on the arm of the microbalance with a platinum wire. Samples were mixture of quartz and graphite having a mass of 100 mg and the molar ratio of C/SiO₂ = 3. Samples were heated to 1 775 K at the rate of 50 K/min in argon flow rate of ~ 50 dcm³/h. Figure 1 shows the essential parts of weight loss curves of test samples. Linear section of the initial rate of weight loss of Quartzite 2 is set in a fairly long period of time, as indicated in Figure 1 with a straight line.

Kinetic experiments show that the reaction in the solid – solid system is inefficient compared to the reaction system between solid-phase – gas. In laboratory studies of SiO₂ + *m*C mixtures the formation of SiC layer on the surface of C was found, which consequently hinders direct contact of SiO₂ particles with particles C. The mechanism of solid – gas reaction (1) can be considered more likely due to the participation of gas phase reaction products, as expressed in equations (2), (3) and (4).

The studied reactions are heterogeneous reactions. In such reactions it is assumed that the reference point is the surface reaction. This surface interface is – in test reaction – between the solid and gas phases, and the two solid phases. In the studied reactions you can speak of at least three areas of interface, and as the reaction proceeds –

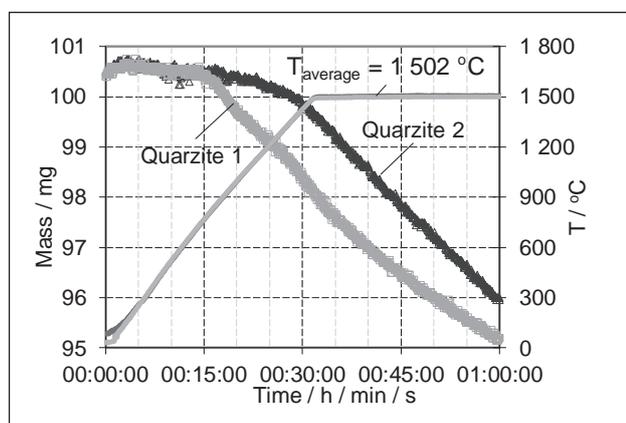


Figure 1 Initial curves of mass loss samples of mixture Quartzite 1 and Quartzite 2 with graphite vs time with mark segment of linear mass loss of Quartzite 2

about four. These three key reactions (2), (3) and (4) extend over the surface of grains of SiO₂ and C. However, values of these surfaces are not known. Nevertheless, being a very rough working hypothesis, which requires subsequent verification, an attempt was made to estimate the order of the surface. This enables the comparison of test results carbothermic reduction of SiO₂ to SiC, referred to the surface of reaction, both to C and SiO₂.

The studies provide average diameter of quartzite and carbon particles. Providing that grains are spheres, the surface of the spheres was calculated and they have been assumed to be the reaction surfaces of carbon and silica grains respectively. The values of these surfaces are summarized in Table 2.

Table 2 Calculated surfaces of Carbon – *Sall_C* and Silica – *Sall_SiO₂*

Investigation	Calculated surface of		C/SiO ₂
	Carbon / cm ²	Silica / cm ²	
Shimoo et al. [2]	7 142,86	495,93	3
Agarwal and Pal [3]	857,14	1 384,62	5
Biernacki and Wozzak [4]	837,55	84,56	1
Sahajwalla et al. [5]	7 190,47	645,30	45
Present study	21,43	7,21	3

Assuming spherical shape of grains has the following justifications: 1) even for compressed pellets it is assumed that [3]: „The particle size for the reactants is uniform and the particles are spherical in shape”, 2) Myrhaug et al. [8] used for modeling the packed bed results of the studies in the form of rate constants and diffusion constants calculated from the shrinking core model, 3) SiC formed in the carbothermic reduction of SiO₂ on the outside of carbon grains may take the shape of a sphere, e.g. [9].

Calculated density of graphite is 2,26 g/cm³ [10–12], measured densities are 2,09 – 2,23 g/cm³ [11, 13]. Density of Carbon Black Thermax N990 is 1,7 – 1,9 g/cm³ [14]. The true density of all black coals is 1,7 – 2,05 g/cm³ [15].

Densities of carbon in the form of graphite or carbon black used in the studies are not quoted. However, the expression for the total surface of spherical particles C – *Sall_C* in a given sample depends on: mass of the sample – *m_sample*, mass fraction of C in the sample – *mass_ratio_C*, particle diameter of C – ϕ_C and density of C – ρ_C , which leads to the following formula:

$$Sall_C = 6 \frac{m_sample \cdot mass_ratio_C}{\phi_C \cdot \rho_C} \quad (5)$$

A similar form expresses a total surface of SiO₂ particles in the shape of a sphere. The spread of parameter values in the samples – study [2–5] and ours – is much greater than possible values of density of graphite dispersion. Sample weights change 50 times, mass fraction C 5,4 times, average particle diameter C 50 times, while the differences between the average values of graphite density and carbon black are $\pm 7\%$. Hence the change

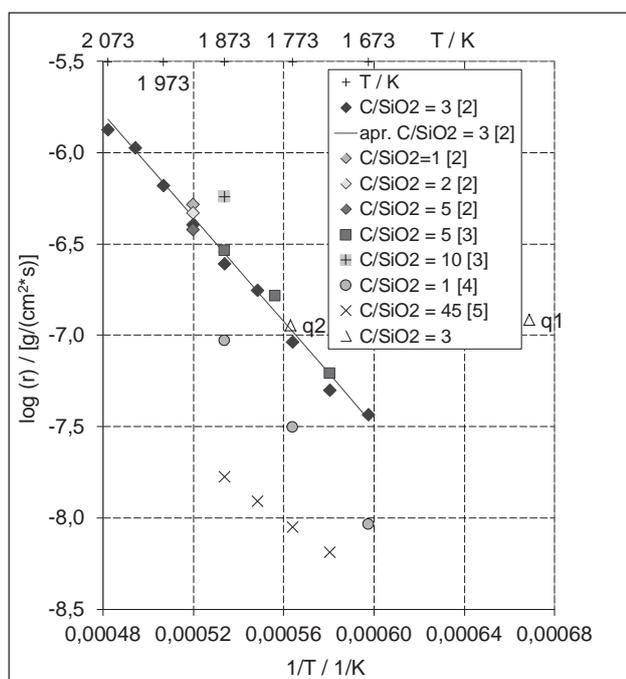


Figure 2 Logarithm of initial rate mass loss of mixture reaction $\text{SiO}_2 + m\text{C}$ divided by surface of C particles vs inverse of temperature; $\log(r) / [\text{g}/(\text{cm}^2 \cdot \text{s})] = f(1/T) / [1/\text{K}]$ from investigations: [2–5] and present study

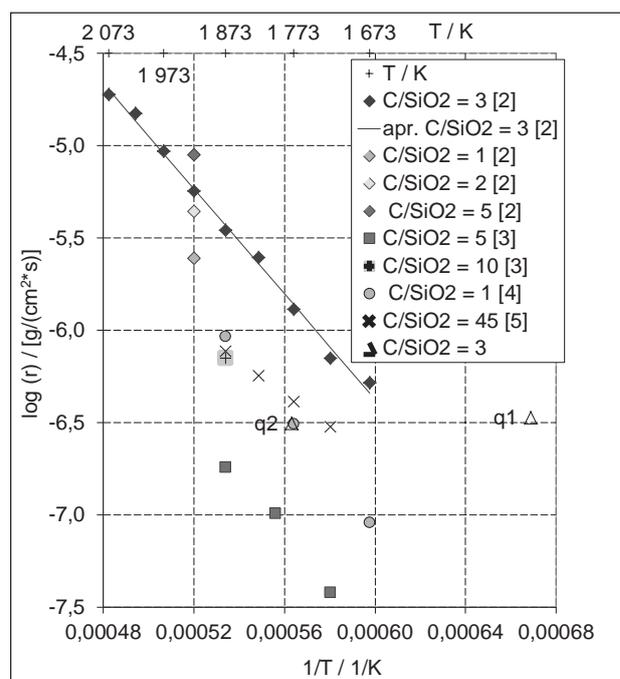


Figure 3 Logarithm of initial rate mass loss of mixture reaction $\text{SiO}_2 + m\text{C}$ divided by surface of SiO_2 particles vs inverse of temperature; $\log(r) / [\text{g}/(\text{cm}^2 \cdot \text{s})] = f(1/T) / [1/\text{K}]$ from investigations: [2–5] and present study

in mass fraction of C, and mass of the particle diameters alters the carbon surface from 38 to 357 times more. So in order to compare the reduction rate with a hypothetical surface density, it was decided to assume both carbon graphite and carbon black of $2,1 \text{ g/cm}^3$.

Taking into account published values, for example [16–18], quartz density of $= 2,6 \text{ g/cm}^3$ was used in calculations.

RESULTS OF COMPARISONS

Initial weight loss rate referenced to a hypothetical surface of C is plotted in Figure 2. There is a certain degree of conformity according to the logarithm of the initial rate of mass loss from various studies of inverse temperature.

The graph in Figure 2 shows that the initial rate of weight loss study [2] – graphite, [3] – carbon black, and the initial sample of own studies – graphite is proportional to the surface of carbon calculated on the assumption that this is the surface of spheres with an average grain diameter. Very high value of molar ratio $\text{C}/\text{SiO}_2 = 45$ and 10 is not part of this trend.

Studies [4] and [5] diverge. Results [4] are derived from studies with variable temperature and reduction rate was estimated from inert mass of approximation to zero. It is generally accepted that research in variable temperatures is not good for the determination of kinetic parameters and it is difficult to compare them with the results of isothermal research [19]. Most come off results are in [5], which relate to samples with very high molar ratio C/SiO_2 because of 45.

The graph (Figure 3) relating to the logarithm of initial rate of weight loss to the surface of SiO_2 does not show the agreement between the results of molar ratio values $\text{C}/\text{SiO}_2 = 1 - 5$, although it can be seen in the results (1 873 K) of two of original $\text{C}/\text{SiO}_2 = 10$ [3] and $\text{C}/\text{SiO}_2 = 45$ [5].

The result of one attempt of isothermal own research may be regarded as defining the order of initial rate of weight loss mixture of $\text{SiO}_2 + m\text{C}$. Initially it can be said that if it does not confirm it, at least it does not exclude the possibility that loosely piled grains as well as compacted ones are subjects of equal research.

CONCLUSIONS

The initial weight loss rate of reaction of silica with carbon derived from various studies was compared. The comparison was made by referring the speed of weight loss of samples to their hypothetical surface, both the surface of C and SiO_2 . It was assumed that the surface of each grain C and SiO_2 is the surface of a sphere of a diameter equal to the average grain diameter and total areas of C and SiO_2 are the sum of the surface of individual grains.

Where reference is the initial rate of weight loss to carbon surface, the comparison reveals high compliance of temperature influence C/SiO_2 at molar ratio of 1 to 5 on the rate of weight loss. For molar ratio C/SiO_2 values 10 and especially 45 there is no such compliance. Indirectly, this is a confirmation that the initial rate of reduction is controlled by the rate of reaction on the surface of carbon.

REFERENCES

- [1] B. Machulec: Teoretyczne podstawy procesu elektrotermicznego wytopu żelazokrzemu oraz krzemu technicznie czystego, *Zeszyty Naukowe Politechniki Śląskiej*, nr 1589, Gliwice 2003, pp. 46-50 and 33-42.
- [2] T. Shimoo, F. Mizutaki, S. Ando and H. Kimura; *Jpn. Inst. Met.*, 52 (1988), 10, 945-953.
- [3] A. Agarwal and U. Pal; *Metallurgical and Materials Transactions B: Process Metallurgy and Materials Processing Science*; 30, (1999), 2, 295-306.
- [4] J. J. Biernacki and G.P. Wozak; *Journal of Thermal Analysis*, 35 (1989), 1651-1667.
- [5] V. Sahajwalla, Ch. Wu, R. Khanna, N. Saha Chaudhury, J. Spink; *ISI International*, 43, (2003) 9, 1309-1315.
- [6] A. G. Vodop'ánov, S.V. Baranov, G.N. Koževnikov; *Izvestiâ Vysših Učebnyh Zavedenij. Cernaâ Metallurgîâ* 3, (1981), 6-9.
- [7] P. G. Loutzenhisser, O. Tuerk, and A. Steinfeld; *Alternative Energy in Materials Processing*, 62 (2010) 9, 49-54; www.tms.org/jom.html
- [8] E. H. Myrhaug, J. K. Tuset, H. Tveit; *Proceedings: Tenth International Ferroalloys Congress; INFACON X: Transformation through Technology*, ISBN: 0-9584663-5-1, 1-4 feb 2004 Cape Town South Africa.
- [9] V. D. Krstic; *J. Am. Ceram. Soc.*, 75 (1992), 1, 170-174.
- [10] W. M. Hess, C.R. Herd, In *Carbon Black*, 2nd ed.; Marcel Dekker: New York, 1993; Chapter 3, p. 149.
- [11] <http://www.mindat.org/min-1740.html> (2014-05-29)
- [12] Entegris, Inc.: Properties and Characteristics of Graphite for semiconductor industry, May 2013; www.entegris.com (2014-05-29).
- [13] Mineralogy Database: Graphite Mineral Data; http://webmineral.com/data/Graphite.shtml#U2qI8fl_tic (2014-05-29).
- [14] Material Safety Data Sheet Carbon Black, CANCARB, Revised Date: Nov. 30, 2011; http://www.continentalcarbon.com/pdfs/Thermal_Black_MSDS.pdf (2014-05-29).
- [15] K. Skoczkowski: *Technologia produkcji wyrobów węglowo-grafitowych*, Śląskie Wydawnictwo Techniczne, Katowice 1995, pp. 48-51 and 173.
- [16] P. Wyszomirski: Surowce mineralne, prezentacja „wyklad-08.pdf”; <http://home.agh.edu.pl/~pwysz/wyklad.htm> (2014-05-29).
- [17] K. Aasly, Thesis for the degree of Phd, Norwegian University of Science and Technology Trondheim, August 2008; <http://www.diva-portal.org/smash/get/diva2:124782/FULLTEXT02.pdf> (2014-05-29).
- [18] CQ - karta techniczna 2013.pdf, Techniart Sp. z o.o. styczeń 2013; www.techniart.pl (2014-05-29).
- [19] J. Plewa: Synteza i badania właściwości nadprzewodników ceramicznych metodami analizy termicznej, *Zeszyty Naukowe Hutnictwo Politechniki Śląskiej* Nr 1641, Gliwice 2004, pp. 113-115.

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