

THE INFLUENCE OF INTENSITY OF ARGON FLOW ON THE RATE OF MASS LOSS IN CARBOTHERMAL REDUCTION OF QUARTZITE TO SILICON CARBIDE

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The effect of argon flow intensity on mass loss rate in the carbothermic reduction of SiO_2 to SiC was examined. The graphite and natural quartzite in a molar ratio of $\text{C}/\text{SiO}_2=3$ were used. Samples were reduced for 6 hours at 1 500 °C. In the range of argon flow intensity from 0,1 to 3,4 dcm^3/min , the high level of rate of mass loss of the sample and the 70 – 80 % of SiC formed in the residue of the sample were obtained.

Key words: silica, carbon, carbothermal, reduction, intensity of argon flow

INTRODUCTION

Very few articles concern the influence of flow rate of inert gas on mass loss of the sample in carbothermic reduction of SiO_2 to SiO, among them for example [1-3].

In the paper by F. K. Van Dijen, R. Metselaar [1] the increase in the flow of He from 0,05 to 0,1 dcm^3/min resulted in a modest increase in the speed reduction. The increase from 0,1 to 0,2 dcm^3/min results in a minimal increase in the rate of weight loss. Whereas, in the paper by C.Y. Chen et al. [2] with an increase in the flow of He from 0,6 to 3 dcm^3/min decreases the yield of SiC and also decreases conversion of SiO and C. The authors of work [2] claim, that the authors of work [1] reported opposite results and gave no explanation of this.

V. Sahajwalla et al. [3] show the influence of intensity of Ar flow on the rate of mass loss such that there is optimum value. Maximum of mass loss is at intensity of Ar flow 1 dcm^3/min . Lower (0,5 dcm^3/min) and higher flows (2 dcm^3/min) make mass loss smaller. This work, however, applies to a relatively low SiO_2 content in the sample (10 % of mass) with very high molar ratio $\text{C}/\text{SiO}_2 = 45$ and in some ways differs from other studies [4].

Therefore, first of all it was decided to investigate the effect of V_{Ar} on the rate sample weight loss in carbothermic reduction of SiO_2 to SiC. The main concern here was not the highest rate of weight loss, rather the rate of argon flow to obtain the biggest possible yield of SiC. Thus, the aim of the research is to find a V_{Ar} intensity to get the greatest amount of SiC in the shortest possible time.

PROCEDURE OF EXPERIMENTS

Investigation of the effect of argon flow rate on mass loss in carbothermic reduction of SiO_2 to SiC was performed in thermobalance “Thermogravimat” type Sartorius 4304. Thermobalance was equipped with vertical tubular reactor of fused Al_2O_3 - “Alsint 99,7” – of inner diameter 27 mm. The reactor has a gas delivery and gas removal to enable directing the gas flow both from top to bottom and reverse. During carbothermic reduction of SiO_2 to SiC (CTR) argon was blown from top to bottom of the reactor with a quartz tube of internal diameter 2,7 mm. The end of the blowing tube was positioned 32,5 cm from the edge of the crucible with the sample. Thermocouple PtRh10-PtRh6 was used to measure the temperature in the reactor.

The analysis of oxygen content in samples was performed on a LECO analyzer ONH836.

The study was conducted with the use of natural quartzite marked BG and graphite from SGL Carbon Group Poland SA Raciborz. Sieve analysis resulted in obtaining quartzite and graphite particles smaller than 63 μm .

Sintered Al_2O_3 crucibles produced by Refractory Materials Branch in Gliwice were used. The dimensions of crucibles: diameter outer/internal 15,2/12,5 mm, height external/internal 18,5/16,94 mm.

Separate components of SiO_2 and C samples were weighed and then subjected to drying at approx. 200 °C for about 2 h. After that time, the components showed no weight loss. Then the components were carefully weighed and divided into samples of molar ratio $\text{C}/\text{SiO}_2 = 3$. Dried and continuously heated ingredients were thoroughly mixed. The portions of samples of 500 mg weighed from the mixture, were then compressed with a force of 161,41 MPa, forming cylindrical pellets having a diameter of 12 mm and a height of about 2,5 mm. Pressed pellets were ejected from the die directly to a previously dried and weighed crucibles. Each sample

with the crucible was dried prior to reduction of about 2 hours, i.e. not appearing until the weight loss. The crucibles with samples were then suspended on a platinum wire rod thermobalance.

Warming the furnace reactor assembly to 1 500 °C, and moving it upwards to close the reactor of thermobalance launch the reduction. Samples were reduced for about 6 h in vertical stream of argon flowing from top to bottom. Turning off the heating and retraction of the furnace to such a height that the sample was in the upper part of the reactor tube being in a stream of argon (this time flowing from bottom to top), stops the reduction. When the temperature dropped to about 200 °C, the sample was removed from the thermobalance suspension. The crucible with the sample was weighed.

Crucibles weight with the samples minus the weight of crucibles themselves are the mass of the samples before reduction, referred to as W^0 . The differences between the mass of crucibles with residue of samples after reduction and the mass of empty crucibles are determined as W^f . Theoretically, W^f is the weight of the residue of the sample after reduction. The loss of mass during the reduction of the sample is $W^0 - W^f$. Due to tumbling, pressing and pushing from the die, initial masses of samples were not exactly the same. In order to compare the weight loss curves of the samples at different flow rates of argon relative mass loss of samples (fractional weight loss) was introduced $(W^0 - W^f) / W^0$.

RESULTS

The resulting weight loss curves of a relative weight loss of the sample $(W^0 - W^f) / W^0$ as a function of reduction time at different values of flow rate of argon at 1 500 °C are shown in Figure 1.

Generally, the higher the intensity of argon flow rate, the higher go the curves (Figure 1). However, there are some exceptions. The curve obtained at the rate of 1,6 dcm³/min runs lower than the curve of 1,2 dcm³/min. Similarly, curves 2,6 and 3,4 dcm³/min go below the curve 2 dcm³/min. While the curve obtained at a flow of 0,1 dcm³/min passes above the curves 0,2 and 0,4 dcm³/min in the range of time reduction. These differences can be regarded as a characteristic of dispersion of results of empirical research. Basically, they do not change the general tendency of increase in weight loss with increasing V_{Ar} . Due to short distances between the curves on the graph in Figure 1, relative mass loss after 360 minutes is shown in Figure 2.

On the surface of some samples there appeared a layer of crust in light grey with a hint of pink or brown. Crust thickness decreased with the increase of argon flow rate. At a flow rate of 2, 2,6, 3,4 dcm³/min the crust is not present or is so thin that it can't be identified. The crust layers were separated from the rest of samples and separately weighed and analyzed for oxygen content.

Weighing the content of crucibles revealed a smaller mass of residue samples W_2^f than W^f resulting from the calculation

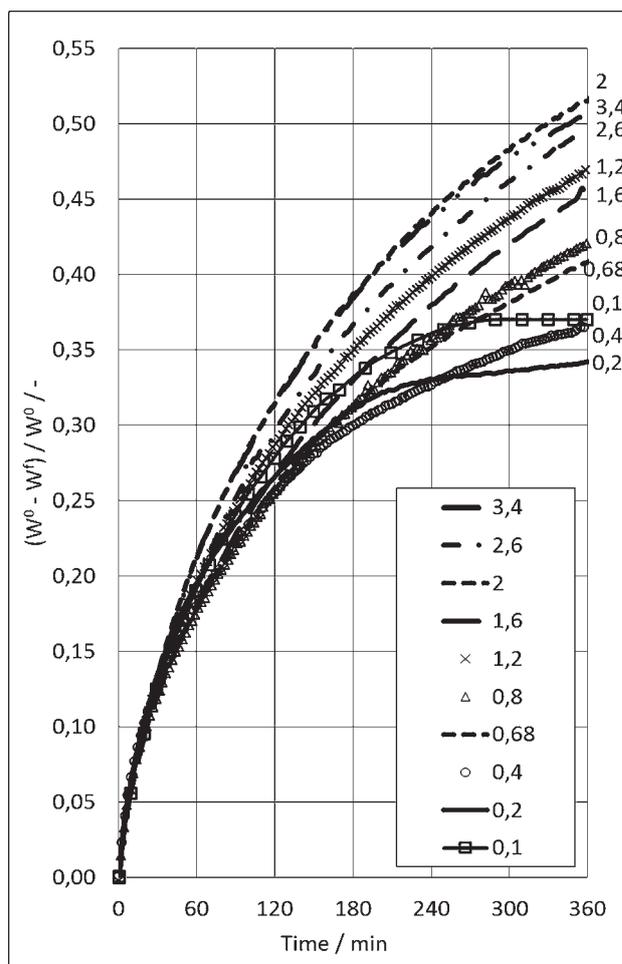


Figure 1 Curves of relative mass loss $(W^0 - W^f) / W^0$ vs time at different intensity of argon flow, V_{Ar} at 1 500 °C

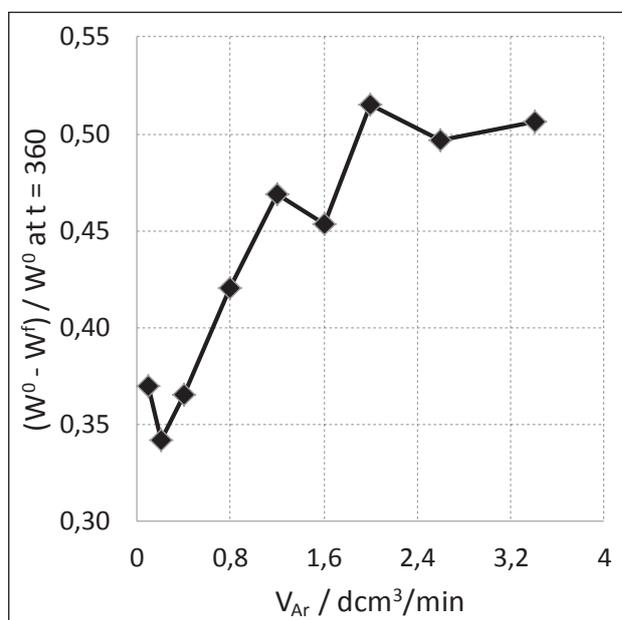


Figure 2 Relative mass loss received at 360 min reduction $(W^0 - W^f) / W^0$ vs intensity of argon flow, V_{Ar}

$$W^f = W^0 - \Delta m \quad (1)$$

At the same time, it turned out that the weight of crucibles after the reduction is greater than the weight of crucibles before the reduction. The mass of this is determined Δm_x .

Between the components of samples (SiO_2 , C, SiC, SiO and CO) and the material of the crucible made of sintered Al_2O_3 a series of reactions is possible, for example [5]. Their detailed analysis is beyond the scope of this article. However, for purposes of the calculation of the mass balance of the sample before and after the CTR, it was formally assumed that SiO escaping from the sample reacts with Al_2O_3 crucible. Hence, the mass of the crust m_{crust} and the difference in weight between the observed loss, W^f , and weighed remnant of the sample W_2^f , and also weight gain crucible, Δmx , are related as follows

$$W^f = W_2^f + m_{\text{crust}} - \Delta mx \quad (2)$$

It is shown in a formal expression of modified mass balance equations, which, briefly are:

$$m_{\text{SiC}}^f + m_{\text{SiO}_2}^f + m_{\text{C}_{\text{Free}}}^f + m_{\text{crust}} + \Delta mx = W^f \quad (3)$$

$$m_{\text{SiO}}^f + m_{\text{CO}}^f = W^0 - W^f \quad (4)$$

Equations (3) and (4) supplemented with balance equations of the number of moles of Si, O, C, and the values of oxygen content in samples, enable to calculate unknown sample mass components. Mass balance system of equations will be presented in detail in the next publication.

Relative proportion of components of the residue mass m_i^f referred to the mass of the sample residue W_2^f , after stopping the reduction after 6 hours is shown in Figure 3. This graph reveals gradual changes of constituents in the residue of the sample with an increase in the flow of argon. Up to the value of 2 dcm^3/min we can observe a clear decrease in SiO_2 , C_{Free} and C_{Tot} content and increase of SiC content. After exceeding 2 dcm^3/min , there are visible fluctuations which do not show a clear tendency. One can discern slight reverse trends, i.e. increase in the content of SiO_2 and C_{Free} and decrease of SiC.

DISCUSSION OF RESULTS

The values of the weight loss achieved referred to the mass of initial sample after 360 min $(W^0 - W^f) / W^0$ (Figure 2), substantially increase with increasing argon flow rate to 2 dcm^3/min .

The data points in Figure 2 suggest that an increase in the rate of weight loss in the reduction of SiO_2 with increasing argon flow rate approaches a certain value. However, it is not known whether it is a global maximum dependence $(W^0 - W^f) / W^0 = f(V_{\text{Ar}})$. This would require further research with even greater V_{Ar} . However, the scope of V_{Ar} used in the present study suggests that, starting with 2 dcm^3/min does not form a crust layer and we obtain a fairly high content of 70 – 80 % SiC of sample residue. This can be considered a rather large value for CTR 6 h at 1 500 °C.

The colour of formed crust layers on the surface of samples in the range of argon flow rate of 0,1 to 1,6 dcm^3/min suggests that it may be a phase comprising SiO_2 . Under the conditions of the experiment the reac-

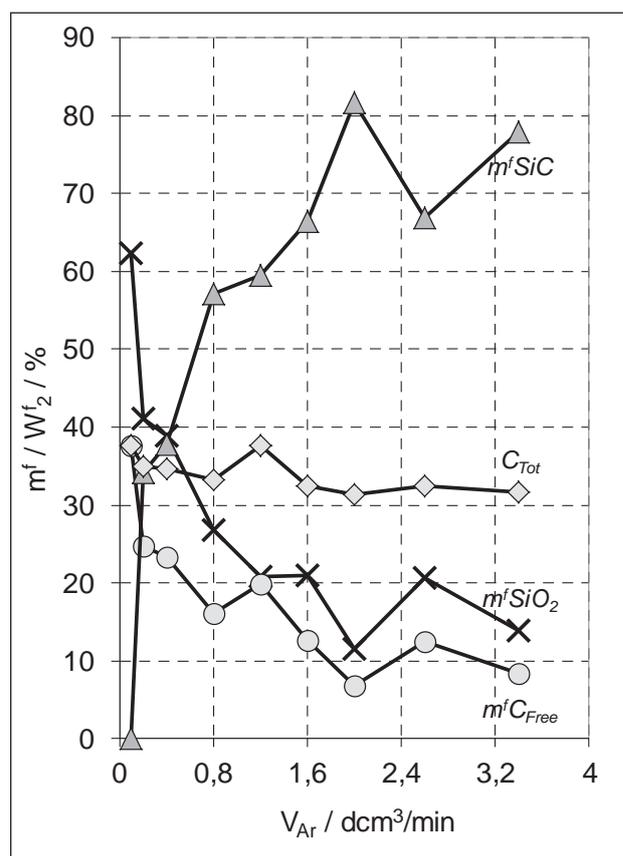


Figure 3 Relative mass content of sample ingredients, m^f / W_2^f , and total carbon content, C_{Tot} vs intensity of argon flow, V_{Ar}

tions $\text{SiO} + 1/2 \text{O}_2 = \text{SiO}_2$ and $2\text{SiO} = \text{Si} + \text{SiO}_2$ are possible [6]. Just as in [7] it was observed, that SiO was condensed and deposited as silicon suboxide, SiO_x , on the surfaces of cooler parts. In the present study SiO_x was condensed on the ends of the wire slings Pt crucible and on the weld of PtRh10 – PtRh6 thermocouple. The oxygen content in mixture of Si + SiO_2 is 36,29 %, and in SiO_2 it is 53,26 %. Under the conditions of this experiment the measured oxygen content in crust layers is maintained at the average level of 52,2 % with a standard deviation of 0,86 %. Such oxygen content suggests that the main component of crust layers is most likely SiO_2 .

The observed mass loss rate and the calculated amount of SiC are a complex function of many parameters of the study. These include properties of mixtures of C + SiO_2 , such as grain size, molar ratio of C/ SiO_2 sample, compression force, and the like, but also geometric conditions of the reactor. The latter refers to the distance from the end of the tube blowing to crucible, height of crucible walls, the shape of the sample and others, which results from, for example test [2] and observations done in this study.

Mass transfer conditions to the sample surface are crucial here. They affect the amount of SiO discharged, as they decide whether or not a crust layer is formed on the sample surface. Crust layer affects the rate of weight loss and the amount of SiC formed in the core sample. With the increase of V_{Ar} the thickness of crust layer de-

creases in such a way that, starting with 2 dcm³/min and above the crust does not form. It can be assumed that with further increase of V_{Ar} the amount of SiC formed may be reduced. However, within the range of V_{Ar} used in this study such a phenomenon did not occur.

CONCLUSIONS

The experiment of carbothermic reduction of SiO₂ to SiC for the intensity of argon flow rate: 0,1, 0,2, 0,4, 0,8, 1,2, 1,6, 2, 2,6, 3,4 dcm³/min was carried out here. Reactions were carried out for 6 hours. After that time the reduction was stopped (though it could be continued).

The study revealed the effect of argon flow intensity on the rate of mass loss of the sample. With the increase of flow rate increases the speed of weight loss of samples. Achieved relative mass loss after 360 min is the largest for argon flow rate 2 dcm³/min. Similar behaviour revealed SiC contents, calculated from mass balance equations on the basis of oxygen content in residue samples. The calculated SiC content requires verification. It can be performed by analyzing the total carbon content, C_{Tot} , which will be the subject matter of the next publication.

Determining the range or a single value of argon flow rate at which maximum created SiC occurs, is a parameter for further carbothermic reaction kinetic studies of SiO₂ to SiC.

LIST OF SYMBOLS

CTR – carbothermic reduction of SiO₂ to SiC

m_{cru}^{before} – mass of crucible before CTR / g

m_{cru}^{after} – mass of crucible after CTR / g

m_{crust} – mass of the crust layer / g

m_i^f – the final mass of the i-th component after stopping the reduction reaction / g

V_{Ar} – intensity flow of argon / dcm³/min

W^0 – initial mass of the sample / g

$(W^0 - W^f) / W^0$ – mass loss achieved relative to the mass of the initial sample / -

W^f – mass of the sample residue after stopping the reduction reaction calculated from the weight loss $W^f = W^0 - \Delta m$ / g, where

$$\Delta m = m_{cru}^{before} + W^0 - (m_{cru}^{before} + W^f) / g$$

$W_2^f = m_{SiC}^f + m_{SiO_2}^f + m_{Cfree}^f$ – mass of residue sample after stopping the reduction reaction, determined from a weighing sample without m_{crust} and Δmx / g

$\Delta mx = m_{cru}^{after} - m_{cru}^{before}$ – mass gain crucible / g

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