

# MASS BALANCE AT PARTIAL RUN OF QUARTZITE CARBOTHERMAL REDUCTION

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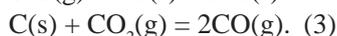
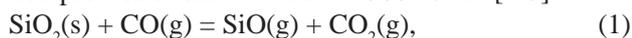
Preliminary Note – Prethodno priopćenje

Mass balance for the process of incomplete carbothermal reduction of  $\text{SiO}_2$  to  $\text{SiC}$  thermogravimetric studies was presented. Tests were performed for the molar ratio of  $\text{C}/\text{SiO}_2 = 3$  at a temperature of  $1\,500\text{ }^\circ\text{C}$  under an argon flow in the range from  $0,1$  to  $3,4\text{ dm}^3/\text{min}$ . Mass balance includes the loss due to escape of  $\text{SiO}$  and the mass of reactants  $\text{C}$  and  $\text{SiO}_2$  due to stopping the reaction. The weight gain of  $\text{Al}_2\text{O}_3$  crucible was found and also the formation of crust layer on the surface of the samples. The crucible weight gain and the weight of crust layer created were taken into account in mass balance.

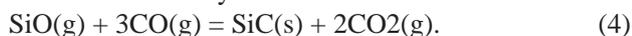
*Key words:* silica, carbon, carbothermal, reduction, mass balance

## INTRODUCTION

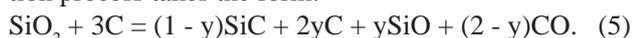
Most likely key reactions in the carbothermal reduction process of silica at about  $1\,500\text{ }^\circ\text{C}$  are [1-3]:



Although some researchers, e.g. [4], take into account the reaction yet



If you take into account  $\text{SiO}$  escaping from the sample during the process in the number of moles equal  $y\text{SiO}$ , summary equation of silica carbothermal reduction process takes the form:

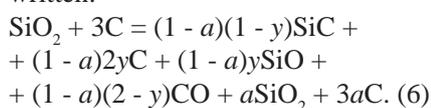


where,  $2y\text{C}$  is the number of moles of carbon which have not reacted due to the escape of  $y\text{SiO}$ .

The summary of the process equation (5) can be seen as an equation, where after running out of  $\text{SiO}_2$ , the reduction is completed and where it is assumed that no amount of moles of  $\text{CO}_2$  leave the system.

## BALANCE WEIGHT AT PARTIAL REACTION

In case of stopping the carbothermal reaction of  $\text{SiO}_2$ , when not all  $\text{SiO}_2$  and/or  $\text{C}$  in a sample of initial weight  $W^0$  have reacted, where  $(1-a)$  and  $a$  are successive moles, which have already reacted and still haven't reacted, the summary of equation of carbothermal reduction process unreacted until the end of silica, can be written:



## EXPERIMENTAL

A detailed description of experimental procedure of thermogravimetric studies of carbothermal reduction of  $\text{SiO}_2$  to  $\text{SiC}$  is shown in [5]. In this study, the difference in weight of sample plus the crucible minus the weight of the crucible is the mass of the sample before the reduction denoted by  $W^0$ . The differences in the weight of crucible with the residue of the sample after reduction and the weight of an empty crucible before reduction were determined as  $W^f$ . Theoretically,  $W^f$  is the weight of the sample residue after the reduction. The loss of sample mass during the reduction is  $W^0 - W^f$ . In order to compare the weight loss curves of samples with unequal initial masses, relative weight loss of samples  $(W^0 - W^f) / W^0$  was introduced.

Taking into account the mass balance of carbothermal reduction of  $\text{SiO}_2$  with respect to: 1) the mass of still unreacted  $\text{SiO}_2$  ( $aN_{\text{SiO}_2}^0 M_{\text{SiO}_2}$ ) and  $\text{C}$  ( $a3N_{\text{C}}^0 M_{\text{C}}$ ), 2) the known weight of sample after stopping the reduction,  $W^f$ , and 3) the known weight loss of sample,  $W^0 - W^f$ , equations can be written as follows:

$$\begin{aligned} &\underbrace{aN_{\text{SiO}_2}^0 M_{\text{SiO}_2}}_{m_{\text{SiO}_2}^f} + \underbrace{(1-a)(1-y)N_{\text{SiC}}^f M_{\text{SiC}}}_{m_{\text{SiC}}^f} + \\ &+ \underbrace{3aN_{\text{C}}^0 M_{\text{C}} + (1-a)2yN_{\text{C}}^f M_{\text{C}}}_{m_{\text{CFree}}^f} = W^f \quad (7) \end{aligned}$$

$$\begin{aligned} &\underbrace{(1-a)yN_{\text{SiO}}^f M_{\text{SiO}}}_{m_{\text{SiO}}^f} + \underbrace{(1-a)(2-y)N_{\text{CO}}^f M_{\text{CO}}}_{m_{\text{CO}}^f} = \\ &= W^0 - W^f \quad (8) \end{aligned}$$

The equation (7) expresses the weight of the sample after stopping the reduction,  $W^f$ , while equation (8) weight loss of the sample,  $W^0 - W^f$ . Furthermore, from

the balance of the number of moles (Si, C, and O) results:

$$N_{SiO_2}^0 = (1-y)N_{SiC}^f + yN_{SiO}^f \quad (9)$$

$$3N_C^0 = (1-y)N_{SiC}^f + 2yN_C^f + (2-y)N_{CO}^f \quad (10)$$

$$2N_{SiO_2}^0 = yN_{SiO}^f + (2-y)N_{CO}^f \quad (11)$$

In equations from (7) to (11) there are unknown numbers of moles of  $N_{SiC}^f$ ,  $N_C^f$ ,  $N_{SiO}^f$ ,  $N_{CO}^f$  and unknown values of  $a$  and  $y$  when the reduction was stopped. Determining the amount of oxygen in the sample after stopping the reduction, enables the calculation of remaining mass of silica,  $M_{SiO_2}$ , in sample and this, in turn, from the first term of equation (7) enables the calculation of  $a$ :

$$m_{SiO_2}^f = aN_{SiO_2}^0 M_{SiO_2} \quad (12)$$

This leaves five unknowns in five equations. This enables the calculation of  $y$  and other masses,  $m_{SiC}^f$ ,  $m_{Cfree}^f$ ,  $m_{SiO}^f$ ,  $m_{CO}^f$ .

### EXPERIMENTAL RESULTS

Studies of carbothermal reduction of  $SiO_2$  revealed that some samples had a crust layer on the surface. The measured mass of crust,  $m_{crust}$ , as a function of flow rate of argon is shown in Figure 1. The formation of crust layer on the surface of the sample takes place under an argon flow in the range from 0,1 to 1,6  $dm^3/min$ . The oxygen content in the sample, and the oxygen content in the crust are shown in Figure 2 graph.

Weighing of trickling crucible contents revealed a lower weight of residue samples,  $W_2^f$ , than that resulting from the mass calculation  $W^f$ ,

$$W_2^f < W^f = W^0 - \Delta m \quad (13)$$

At the same time, it turned out that masses of crucibles after reduction are bigger than the weights of crucibles before reduction.

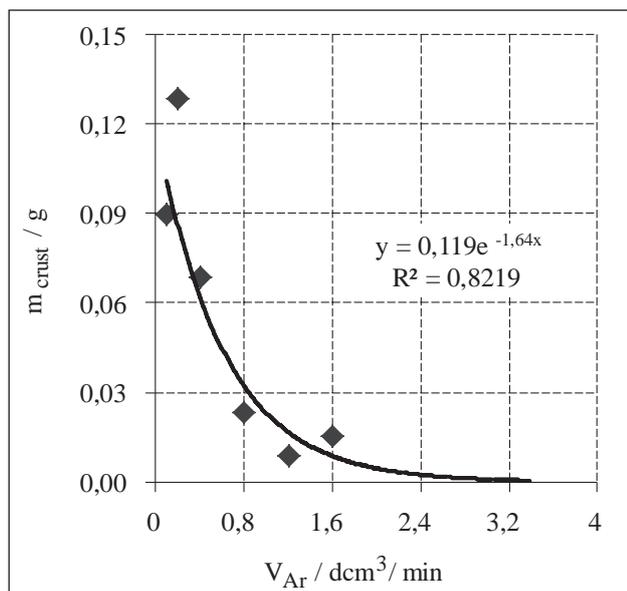


Figure 1 Mass of upper layer of crust,  $m_{crust}$  in samples vs intensity of argon flow,  $V_{Ar}$

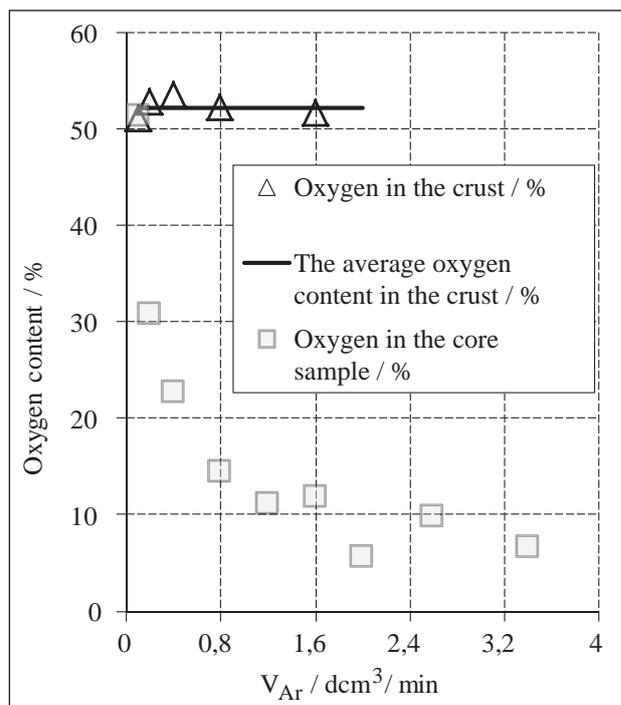


Figure 2 Oxygen content in core sample and in upper layer of crust vs intensity of argon flow,  $V_{Ar}$

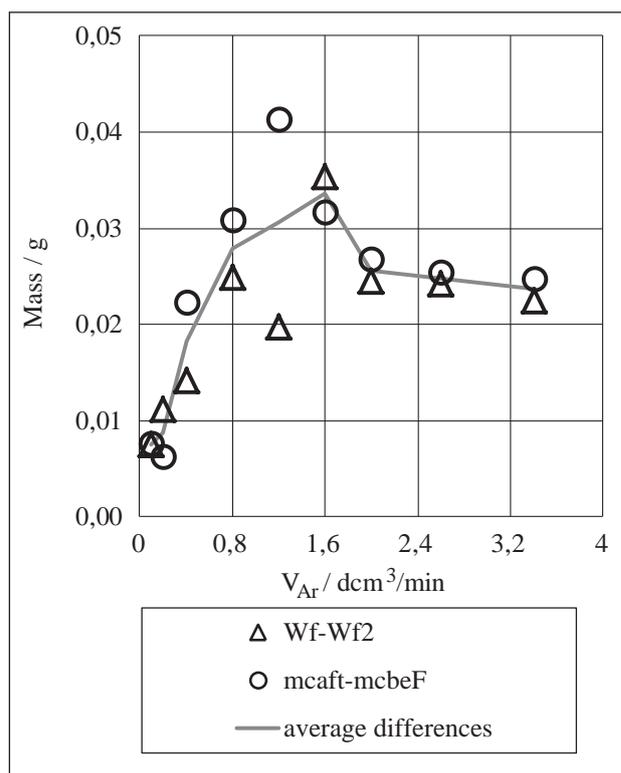


Figure 3 Comparison of differences  $W^f - W_2^f$  with differences of mass of crucibles before and after CTR  $m_{cru}^{before} - m_{cru}^{after}$  vs intensity of argon flow ( $V_{Ar}$ )

The comparison of differences in masses  $W^f - W_2^f$  and the comparison of differences of masses of crucibles  $m_{cru}^{after} - m_{cru}^{before}$  are shown in Figure 3. This graph shows that these differences reach approximately similar values. Hence, it can be assumed that part of mass samples penetrated into crucibles, e.g. by diffusion of  $SiO$  to the floors and walls of  $Al_2O_3$  crucibles.

Quantities: weight gain crucibles,  $\Delta mx$ , mass of the crust,  $m_{crust}$ , the difference between the calculated mass of the residue of sample,  $W^f$ , and the weighed residue of the sample,  $W_2^f$ , are related as follows:

$$W^f = W_2^f + m_{crust} + \Delta mx. \quad (14)$$

Taking into account equation (14) in equation (7) leads to a modified mass balance equation:

$$\begin{aligned} & aN_{SiO_2}^0 M_{SiO_2} + (1-a)(1-y)N_{SiC}^f M_{SiC} + \\ & + 3aN_C^0 M_C + (1-a)2yN_C^f M_C + \\ & + m_{crust} + \Delta mx = W^f. \end{aligned} \quad (15)$$

Equation (15) together with equations (8), (9), (10) and (11) is a system of equations of mass balance and the number of moles in the carbothermal reduction of  $SiO_2$  to  $SiC$ . These equations were solved using nonlinear programming in a spreadsheet using the Solver. The results of these calculations in the form of relative mass content of samples ingredients,  $m_i^f/W_2^f$ , vs the intensity of argon flow,  $V_{Ar}$ , are presented in a previous article.

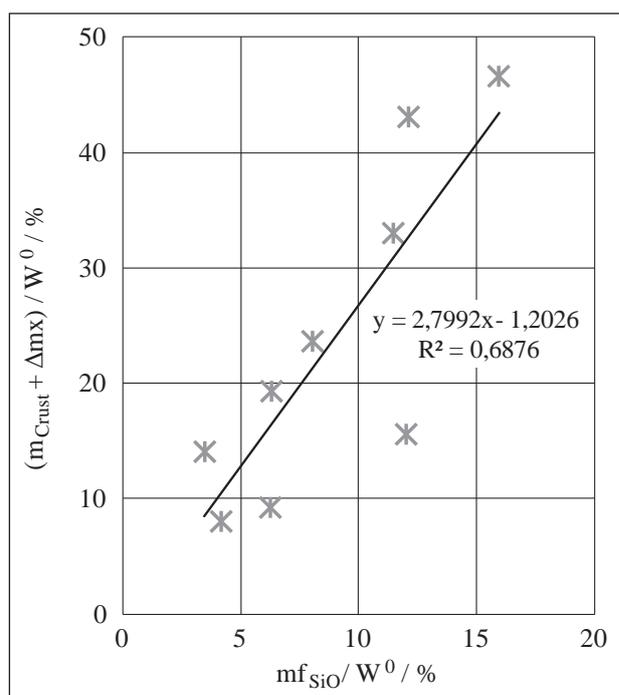
## DISCUSSION OF RESULTS

During the studies the following phenomena were observed: 1) formation of crust layer on the surface of a sample, 2) incompatibility of the calculated mass of the residue of a sample and the weighed sample, and 3) increase in the weight of a crucible.

Under the conditions of the experiment the reactions  $SiO + 1/2 O_2 = SiO_2$  and  $2SiO = Si + SiO_2$  are possible [6]. In the experiment [7] carried out at higher temperature, it has been established that the crust formation is a mixture of  $Si$  and  $SiO_2$ . The oxygen content in the crust is approximately constant, remaining at an 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 thickness and the mass of resulting crust decreases with the increase of argon flow intensity (Figure 1). Starting with value 2  $dm^3/min$ , and higher, it practically disappears. This may mean that the mass transfer in the gas phase intensifies with increasing intensity of argon flow rate. Elution of reaction products in gas phase at 2  $dm^3/min$  and above is so large that such a layer is not formed. A similar effect was observed in the slag reduction studies [8], where the changes in gas flow rate and the distance of the end of the gas discharge pipe from the surface of the slag affected the formation of crust layer.

The difference in weight  $W^f - W_2^f$  is significantly compensated by the increase in the weight of crucible after reduction in relation to its weight before the reduction. This means that some products or reactants may react with  $Al_2O_3$  crucible. 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 [9]. Leaving this issue behind,



**Figure 4** Comparing the sum of masses of crust layers and increases of masses of crucibles with relative  $SiO$  masses produced

it was assumed that in the equation of balance of components of the sample after stopping the reaction, part of gaseous product in the form of  $SiO$  reacts with a crucible or is deposited on it.

Partial confirmation of this view is a correlation, the sum of masses of the crust  $m_{crust}$  and the increase in mass crucibles  $\Delta mx$  with the masses of generated  $SiO$ ,  $m_{SiO}^f$ . The correlation as referred to the mass  $W^0$  is shown in Figure 4.

The measured experimental parameters reveal a certain scattering of values appearing in the research. It is a typical phenomenon of empirical measurement values. Particularly, however, considerable inaccuracy is caused by crust weight and mass of sample residue. The weighing process is subject to considerable inaccuracy, because despite all the elaborate care it was difficult to collect the entire crust, and together with the collected pieces of crust a certain amount of the rest of the sample was collected. However, this inaccuracy decreases as the mass of the crust decreases and disappears in samples without crust.

## CONCLUSIONS

The mass of the crust decreases with increasing argon flow rate. In geometrical conditions of the reactor used in the study - practically it does not occur at the 2  $dm^3/min$  or more. The oxygen content in the crust is approximately constant with a value suggesting that the main component of the crust is  $SiO_2$ .

The oxygen content in the core sample decreases with increasing intensity of argon flow.

The resulting equations are suitable for the mass balance of every uncompleted and completed carbothermal

reaction of  $\text{SiO}_2$  to  $\text{SiC}$ , both when there is a residue on the surface of samples in the form of crust and the weight gain of the crucible. Hence the resulting equations can be used to analyze balance weight of partially reduced samples at various stages of achieved reduction.

## LIST OF SYMBOLS

$a$  – the number of unreacted moles due to stopping the reduction reaction

CTR – Carbothermal Reduction of  $\text{SiO}_2$  to  $\text{SiC}$

$M_i$  – molar mass of  $i$ -th component / g/mol

$m$  – mass / g

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

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

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

$N_i^0$  – the initial number of moles of the  $i$ -th component

$N_i^f$  – the final number of moles of the  $i$ -th component after stopping the reduction reaction

$V_{Ar}$  – intensity of argon flow /  $\text{dcm}^3/\text{min}$

$W^0$  – initial mass of the sample / g

$(W^0 - W^f) / W^0$  – weight 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

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

$W_2^f$  – weight of residue sample after stopping the reduction reaction determined from a sample weighing sprinkled (without the weight of the crust  $m_{crust}$ ) / g

$y$  – the number of unreacted moles due to the escape of  $\text{SiO}$

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**Note:** The responsible translator for English language is Jadwiga Węgrzyn, MA, Senior Lecturer, the Silesian University, Katowice, Poland