Mass balance for the process of incomplete carbothermal reduction of SiO\textsubscript{2} to SiC thermogravimetric studies was presented. Tests were performed for the molar ratio of C/SiO\textsubscript{2} = 3 at a temperature of 1 500 °C under an argon flow in the range from 0,1 to 3,4 dm\textsuperscript{3}/min. Mass balance includes the loss due to escape of SiO and the mass of reactants C and SiO\textsubscript{2} due to stopping the reaction. The weight gain of Al\textsubscript{2}O\textsubscript{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 °C are [1-3]:

\begin{align*}
\text{SiO}_2(s) + \text{CO}(g) &= \text{SiO}(g) + \text{CO}_2(g), \quad (1) \\
\text{SiO}(g) + 2\text{C}(s) &= \text{SiC}(s) + \text{CO}(g), \quad (2) \\
\text{C}(s) + \text{CO}_2(g) &= 2\text{CO}(g). \quad (3)
\end{align*}

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

\begin{equation}
\text{SiO}(g) + 3\text{CO}(g) = \text{SiC}(s) + 2\text{CO}_2(g). \quad (4)
\end{equation}

If you take into account SiO escaping from the sample during the process in the number of moles equal \( y \) SiO\textsubscript{2}, summary equation of silica carbothermal reduction process takes the form:

\begin{equation}
\text{SiO}_2 + 3\text{C} = (1 - a) (1 - y)\text{SiC} + 2\text{C} + y\text{SiO} + (2 - y)\text{CO}. \quad (5)
\end{equation}

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

The summary of the process equation (5) can be seen as an equation, where after running out of SiO\textsubscript{2}, the reduction is completed and where it is assumed that no amount of moles of CO\textsubscript{2} leave the system.

BALANCE WEIGHT AT PARTIAL REACTION

In case of stopping the carbothermal reaction of SiO\textsubscript{2}, when not all SiO\textsubscript{2} and/or 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:

\begin{align*}
\text{SiO}_2 + 3\text{C} &= (1 - a)(1 - y)\text{SiC} + \\
&+ (1 - a)(2 - y)\text{CO} + a\text{SiO}_2 + 3a\text{C}. \quad (6)
\end{align*}

EXPERIMENTAL

A detailed description of experimental procedure of thermogravimetric studies of carbothermal reduction of SiO\textsubscript{2} to 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 \( W^\prime \). Theoretically, \( W^\prime \) is the weight of the sample residue after the reduction. The loss of sample mass during the reduction is \( W^0 - W^\prime \). In order to compare the weight loss curves of samples with unequal initial masses, relative weight loss of samples \( \frac{W^0 - W^\prime}{W^0} \) was introduced.

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

\begin{align*}
\frac{a N_{	ext{SiO}_2}^0 M_{	ext{SiO}_2} + (1 - a)(1 - y) N_{\text{SiC}}^0 M_{\text{SiC}} +}{m_{\text{SiO}_2} + m_{\text{SiC}}} + \\
\frac{3a N_{\text{C}}^0 M_{\text{C}} + (1 - a)(2 - y) N_{\text{CO}}^0 M_{\text{CO}} = W^\prime}{m_{\text{Cfree}}}
\end{align*}

\begin{align*}
(1 - a) y N_{\text{SiO}_2}^0 M_{\text{SiO}_2} + (1 - a)(2 - y) N_{\text{CO}}^0 M_{\text{CO}} = \\
\frac{m_{\text{SiO}_2}}{m_{\text{Cfree}}} + \frac{m_{\text{CO}}}{m_{\text{Cfree}}}
\end{align*}

\begin{align*}
W^0 - W^\prime &= \frac{m_{\text{SiO}_2}}{m_{\text{Cfree}}} + \frac{m_{\text{CO}}}{m_{\text{Cfree}}}. \quad (8)
\end{align*}

The equation (7) expresses the weight of the sample after stopping the reduction, \( W^\prime \), while equation (8) weight loss of the sample, \( W^0 - W^\prime \). Furthermore, from
the balance of the number of moles (Si, C, and O) results:

\[ N_{SiO_2}^d = (1 - y)N_{SiO_2}^f + y N_{SiO_2}^o \]  
\[ 3N_C^d = (1 - y)N_C^f + 2y N_C^o + (2 - y)N_C^{CO} \]  
\[ 2N_{SiO_2}^o = y N_{SiO_2}^o + (2 - y)N_C^{CO} \]

In equations from (7) to (11) there are unknown numbers of moles of \( N_{SiO_2}^f \), \( N_C^f \), \( N_{SiO_2}^o \), \( N_C^{CO} \) 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 \( a \):

\[ m_{SiO_2} = a N_{SiO_2}^o M_{SiO_2} \]

This leaves five unknowns in five equations. This enables the calculation of \( y \) and other masses, \( m_{SiO_2} \), \( m_{SiO_2} \), \( m_{SiO_2} \), \( m_{CO} \).

**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, \( W_f' \), than that resulting from the mass calculation \( W_f \):

\[ W_f' < W_f = W_o - \Delta m. \]

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

The comparison of differences \( W_f' - W_f \) and the comparison of differences of masses of crucibles \( m_{crust} - m_{crust} \) 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\(_2\)O\(_3\) crucibles.
Quantities: weight gain crucibles, $\Delta m_x$, mass of the crust, $m_{\text{crust}}$, the difference between the calculated mass of the residue of sample, $W_0^f$, and the weighed residue of the sample, $W_2^f$, are related as follows:

$$W_0^f = W_2^f + m_{\text{crust}} + \Delta m_x \quad (14)$$

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

$$a'N_{\text{SiO}}^0 M_{\text{SiO}} + (1 - a)(1 - y)N_{\text{SC}}^0 M_{\text{SC}} + 3aN_{\text{C}}^0 M_{\text{C}} + (1 - a)2yN_{\text{C}}^0 M_{\text{C}} + m_{\text{crust}} + \Delta m_x = W_0^f. \quad (15)$$

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 $\text{SiO}_2$ to $\text{SiC}$. 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, $m_{\text{SiO}}^i / W_0^f$, vs the intensity of argon flow, $V_{\text{Ar}}$, 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 $\text{SiO} + \frac{1}{2}\text{O}_2 = \text{SiO}_2$ and $2\text{SiO} = \text{Si} + \text{SiO}_2$ are possible [6]. In the experiment [7] carried out at higher temperature, it has been established that the crust formation is a mixture of $\text{Si}$ and $\text{SiO}_2$. 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 $\text{SiO}_2$.

The thickness and the mass of resulting crust decreases with the increase of argon flow intensity (Figure 1). Starting with value 2 dcm$^3$/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 dcm$^3$/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 $W_0^f - W_2^f$ 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 $\text{Al}_2\text{O}_3$ crucible. Between the components of samples ($\text{SiO}_2$, $\text{C}$, $\text{SiC}$, $\text{SiO}$ and $\text{CO}$) and the material of the crucible made of sintered $\text{Al}_2\text{O}_3$, a series of reactions is possible, for example [9]. Leaving this issue behind, 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 $\text{SiO}$ reacts with a crucible or is deposited on it.

Partial confirmation of this view is a correlation, the sum of masses of the crust $m_{\text{crust}}$ and the increase in mass crucibles $\Delta m_x$ with the masses of generated $\text{SiO}$, $m_{\text{SiO}}$. The correlation as referred to the mass $W_0^f$ 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 dcm$^3$/min or more. The oxygen content in the crust is approximately constant with a value suggesting that the main component of the crust is $\text{SiO}_2$.

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 reduction.
reaction of SiO₂ to 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 sam-
ple at various stages of achieved reduction.

LIST OF SYMBOLS

\( a \) – the number of unreacted moles due to stoping the
reaction reaction

\( \text{CTR} \) – Carbothermal Reduction of SiO₂ to SiC

\( M_i \) – molar mass of i-th component / g/mol

\( m \) – mass / g

\( m_{\text{before}} \) – mass of crucible before CTR / g

\( m_{\text{after}} \) – mass of crucible after CTR / g

\( m_f \) – the final mass of the i-th component, after stop-
ing the reduction reaction / g

\( N_i^0 \) – the initial number of moles of the i-th compo-
nent

\( N_i' \) – the final number of moles of the i-th compo-
nent after stopping the reduction reaction

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

\( W^0 \) – initial mass of the sample / g

\( (W^0 - W') / W^0 \) – weight loss achieved relative to the
mass of the initial sample / -

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

\( \Delta m = m_{\text{before}} + W^0 - (m_{\text{after}} + W_f) \)

\( W_{\text{crust}} \) – weight of residue sample after stopping the re-
duction reaction determined from a sample
weighing sprinkled (without the weight of the
\( y \) – the number of unreacted moles due to the es-
cape of SiO

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