J. WĘGRZYN, A. MOŚCICKI, T. BORECKI

ISSN 0543-5846
METABK 56(1-2) 51-54 (2017)
UDC – UDK 661.68.665:66.094.3:669.9:66.094.1:311.11=111

DETERMINATION OF THE CONTENT OF SILICON CARBIDE BY MASS BALANCE AND ANALYSIS OF OXYGEN AND CARBON CONTENT

Received – Primljeno: 2016-09-29
Accepted – Prihvaćeno: 2016-11-25
Original Scientific Paper – Izvorni znanstveni rad

The paper presents the results of calculations of silicon carbide content in residue samples of carbothermic reduction of SiO_2 after 6 hours. The content of SiC was calculated in two ways. The first from mass balance equations of samples and analysis of oxygen content. The second from analysis of oxygen and total carbon content. The values calculated by the two methods are similar. The total and free carbon content was determined according to procedures described in PN-EN ISO 21068-2:2010P and additional free carbon content at temperatures higher than recommended by the standard. The sum of calculated values of SiO_2 and SiC contents revealed measured excess of free carbon content.

Key words: silicon carbide content, oxygen analysis, reduction, carbon analysis, mass balance

INTRODUCTION

The subject of analysis were samples from carbothermic reduction reaction of SiO_2 after 6 hours. [1]. The total reaction of silica with carbon molar ratio of 1:3 can be as follows

$$SiO_2 + 3C = SiC + 2CO \quad (1)$$

However, during this reaction a certain number of ySiO moles escape [1, 2]. Consequently, the amount of SiC formed may vary depending on the number of ySiO moles, that escaped (forever).

While the determination of oxygen content poses no significant problems, the determination of total and/or free carbon content, by combustion analysis, may be difficult or even impossible [3]. There appear many difficulties associated with the sample's morphology, size and form of precipitation of carbon – silicon carbide system [3 - 8]. Therefore, taking under consideration the results of calculation of the mass balance of the sample components with an additional emphasis on the results of the analysis of the oxygen content enables more likely estimation of silicon carbide content, than would it result from the analysis of total and free carbon in tested samples.

OXYGEN AND TOTAL CARBON ANALYSIS

The analysis of oxygen content in samples was performed on a LECO analyzer ONH836 according to the procedure provided by the manufacturer. The analysis of carbon content in samples was performed on ELTRA analyzer CHS 900 Helios. Total carbon content and carbon free was determined by the procedures described in PN-EN ISO 21068-2:2010P [9]. Carbon-free content at a temperature higher than the norm indicated was also determined.

The source of silica was quartzite of grain size ≤ 63 μm. As a reducer carbon graphite of grain size ≤ 63 μm was also used.

The results of analysis of oxygen content % O measured and % O calculated from mass balance are shown in Figure 1. There is a similarity between measured and calculated values. The relation between % O calculated

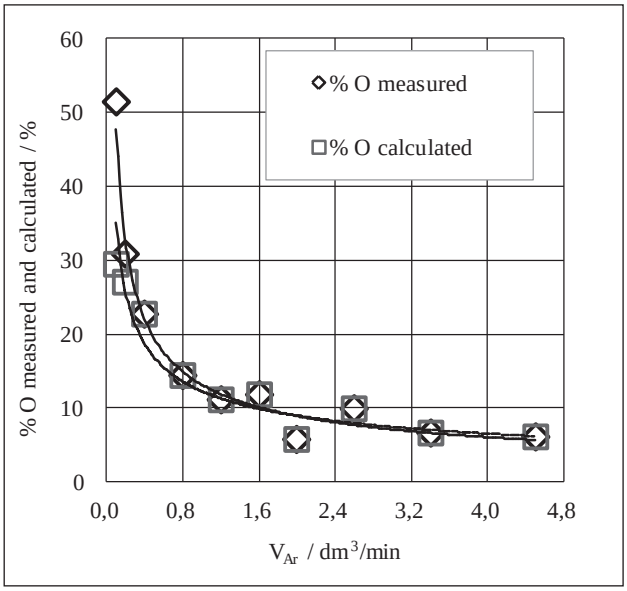

Figure 1 The results of oxygen content analysis, % O measured and calculated from mass balance, % O calculated vs intensity of argon flow, V_{Ar}

J. Węgrzyn, A. Mościcki - Silesian University of Technology, Faculty of Materials Engineering and Metallurgy, Katowice, Poland, T. Borecki - Central Mining Institute, Department of Environmental Monitoring, Katowice, Poland

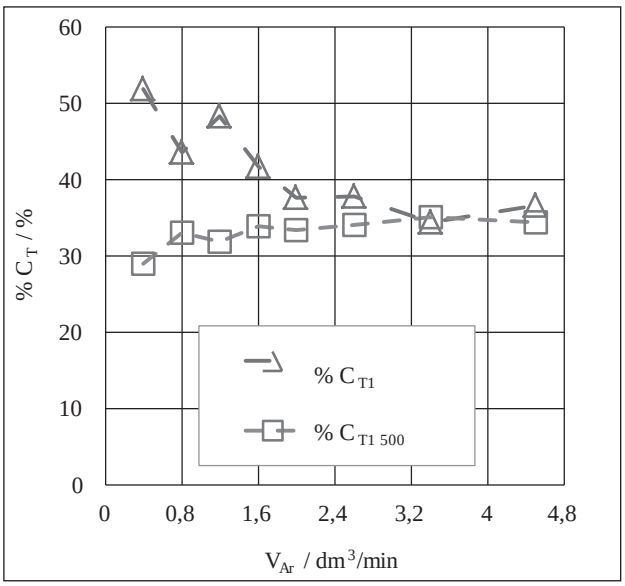

Figure 2 The results of total carbon content analysis calculated from mass balance taking into account the analysis of the oxygen, % C_{T1} and measured % $C_{T1\ 500}$ vs intensity of argon flow, V_{Ar}

= f (% O measured) – not shown – has a coefficient R^2 = 0,8805.

The results of analysis of total carbon content determined in the temperature 1 500 °C, % $C_{T1\ 500}$ and the results calculated from mass balance, taking into account the analysis of oxygen content % C_{T1} are shown in Figure 2.

The average absolute difference is 3,76 % with a standard deviation of 3,99 %. The dependence % C_{T1} = f (% $C_{T1\ 500}$) – not shown – has a coefficient of R^2 = 0,8655.

The calculations assume formal simplifying assumption, that the sample contains only SiO_2, SiC and C. SiC content was calculated in two ways. The first, designated % 1_SiC, based on the calculations of mass balance, taking into account the analysis of oxygen content. The second, designated % 2_SiC, based on the results of oxygen analysis (which allows to calculate silica content, % SiO_2) and results of total carbon analysis % $C_{T1\ 500}$, based on derived equation

$$\%\ 2\_SiC = (100\ \% - \%\ SiO_2 - \%\ C_{T1\ 500}) \frac{M_{SiC}}{M_{Si}} \quad (2)$$

For the calculation of SiC according to (2) it is not necessary to know the content of free carbon.

Compared contents of SiC % 1_SiC with contents % 2_SiC are shown in Figure 3 and Figure 4. Average absolute differences between values % 1_SiC and % 2_SiC is 5,38 % with a standard deviation of 6,04 %. The values % 1_SiC and % 2_SiC in function V_{Ar} (Figure 3) change by the same trends. The degree of matching of the regression line in relation % 2_SiC = f (% 1_SiC) (Figure 4) is R^2 = 0,9103.

This shows the possibility of calculating the content of SiC on the basis of mass balance calculations, without the analysis of total carbon.

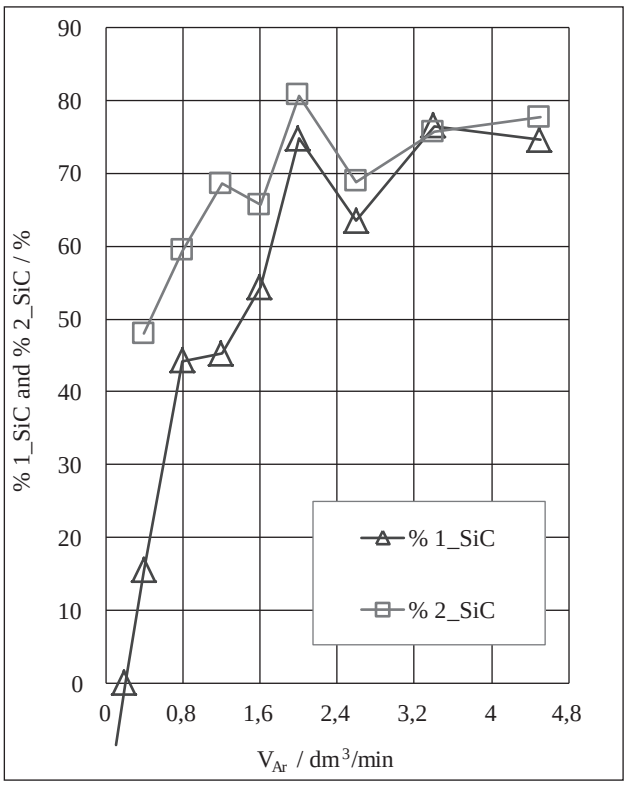

Figure 3 Comparison of SiC content calculated from mass balance, taking into account analysis of oxygen, % 1_SiC with SiC content calculated from the results of analysis of oxygen and total carbon, % 2_SiC vs intensity of argon flow, V_{Ar}

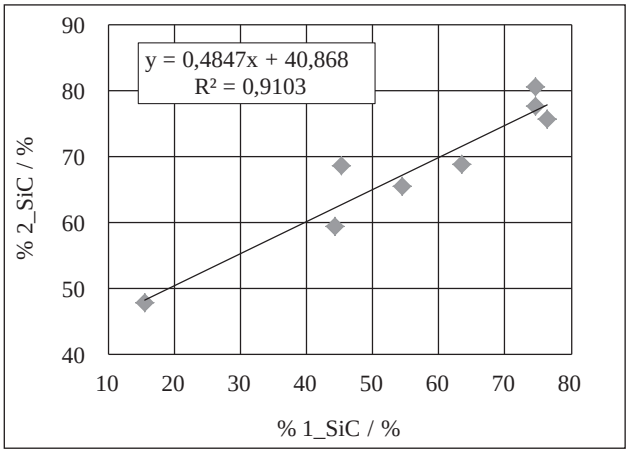

Figure 4 Contents of SiC calculated from the results of analysis of oxygen and total carbon, % 2_SiC vs calculated from the mass balance, taking into account the analysis of oxygen, % 1_SiC

CARBON FREE ANALYSIS

In the study of carbon-free content in the reference sample of silicon carbide [10] in the analyser ELTRA with the requirements of PN-EN ISO 21068-2:2010P [9] at 850 °C too low content of carbon-free in relation to a specified contents of the reference sample was found. Increasing the temperature to 1 350 °C led to the display content compatible with the reference value. However, determined at 1 350 °C, the content of carbon-free in the samples tested tend to be too large.

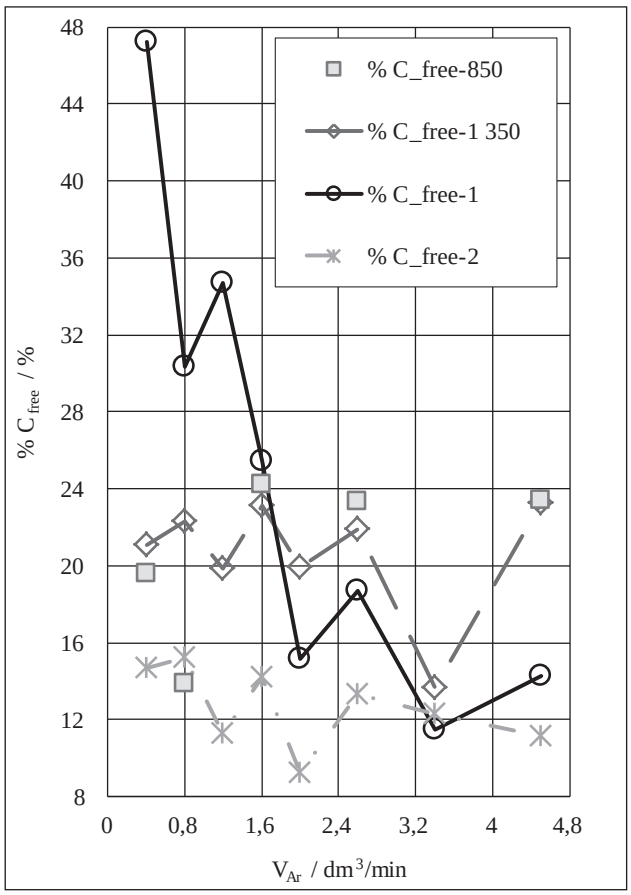

Figure 5 Measured and calculated contents of free carbon vs intensity of argon flow, V_{Ar}

Measurements performed at the temperature prescribed by the standard (850 °C) also show too high values of free carbon, close to the value of 1 350 °C.

Figure 5 shows measured and calculated contents of free carbon, where the values % $C_{free\text{-}850}$ and % $C_{free\text{-}1\ 350}$ are measured at temperature 850 °C and 1 350 °C respectively, and the values % $C_{free\text{-}1}$ and % $C_{free\text{-}2}$ are calculated. % $C_{free\text{-}1}$ is calculated based on values of m_C^f calculated from equations of mass balance and measured W_2^f

$$\% C_{free\text{-}1} = \frac{m_C^f}{W_2^f} 100\,\% \qquad (3)$$

Whereas, % $C_{free\text{-}2}$ is calculated from relation using the values contained in formula (2) as follows:

$$\% C_{free\text{-}2} = (100\,\% - \% SiO_2 - \% 2\ SiC) \qquad (4)$$

The average values of free carbon are measured % $C_{free\text{-}850}$ = 20,86 %, % $C_{free\text{-}1\ 350}$ = 20,64 % and calculated % $C_{free\text{-}1}$ = 24,66 %, % $C_{free\text{-}2}$ = 12,67 % respectively. Measured values do not show a downward trend with increasing V_{Ar}. If together with the increase of V_{Ar} decreases the content of SiO_2 and increases the content of SiC, no matter how it was calculated, the content of some measured free carbon should reveal a downward trend but it does not. In such a situation, it was decided to designate free carbon as a result of the calculation.

DISCUSSION

In composite C/SiC presence of protective layer of silicon carbide, on the interface of the fiber-matrix, is the cause of improvement of oxidation resistance, as it was found in the paper T. Gumuła, S. Błażewicz [4]. T. Shimoo et al. [5] state that perfect coverage with silicon carbide is necessary to inhibit the oxidation of composite fiber. From that it appears that increasing the oxidation resistance may indicate an obstacle in the combustion of free carbon, if it is covered with SiC.

Research of Y. Hui-Mei et al. [6] of thermal stability of nano-SiC powders with an excess of free carbon allows authors to conclude that for complete removal of free carbon the temperature treatment of nano-SiC should be about 750 °C in air. This value is lower than 850 °C required by the PN-EN ISO 21068-2:2010P [9] for the determination of carbon-free content.

In study [5] it was found that carbon could not be detected by X-ray diffraction, because it was thickly covered with SiC. Similarly it was found [6], that XRD analysis of nano-SiC powders do not show in the results of the phase of carbon. However, C. Czosnek and J.F. Janik [3] based on coarse XRD studies, stating that after the additional pyrolysis at 1 650 °C free carbon has been crystallized enough to cause X-ray diffraction. Authors [3] remarked on a noteworthy problem of detecting small amounts of free carbon in the powders of carbon - silicon carbide. Typical combustion analysis carries the risk of oxidation of highly reactive nanoparticles SiC [3]. If free carbon is occluded in amorphous SiO_xC_y, then it cannot be analyzed [3].

The factor determining the temperature of free carbon combustion is its morphology. An example of such influence of this factor on combustion temperature is shown in the work A. Huczko et al. [7]. The results of thermogravimetric analysis of controlled combustion of silicon carbide of microcrystalline morphology and nanofibers SiC were compared. The combustion of micrometer SiC powder begins at temperature above 1 100 °C. The analysis of combustion nanofibers SiC indicates that the process of combustion of free carbon occurs at the temperature of approx. 550 °C. Combustion of nanofibers SiC begins at about 800°C. This value corresponds well with the value of 750 °C from work [6] postulated to complete removal of free carbon from nano-powder of SiC. Furthermore, from [7] it results that the combustion temperature difference of micro- and nanostructures SiC reaches 300 °C.

CONCLUSIONS

Simplified calculations of all the products of the sample after incomplete carbothermic reduction reaction can be carried out based on mass balance equations. Then the results of the analysis of oxygen content are useful.

The results of analysis of total carbon content enable to determine the content of SiC without using mass bal-

ance equations. The content of SiC determined in this way is close to the value of SiC defined from calculation of mass balance equations.

LIST OF SYMBOLS

% 1_SiC – SiC content calculated from mass balance, taking into account the analysis of oxygen content wt. %,

% 2_SiC – SiC content calculated from the results of the analysis of oxygen and total carbon according to equation (2), wt. %,

% C_{free-1} – content of free carbon calculated from mass balance, taking into account the analysis of oxygen content according to equation (3), wt. %,

% C_{free-2} – content of free carbon calculated from equation (4), wt. %,

% $C_{free-850}$ – content of free carbon measured in temperature 850 °C, wt. %,

% $C_{free-1\ 350}$ – content of free carbon measured in temperature 1 350 °C, wt. %,

% C_{T1} – total carbon content calculated from mass balance, taking into account the analysis of oxygen content, wt. %,

% $C_{T1\ 500}$ – total carbon content measured in temperature 1 500 °C, wt. %,

% O calculated – content of oxygen in sample calculated from equations of mass balance, wt. %,

% O measured – content of oxygen in sample measured from oxygen analysis, wt. %,

% SiO_2 – content of silica, wt. %,

m_i^f – final mass *i*-th component after stopping reaction reduction, g,

M_i – molar mass of *i*-th component, g/mole,

V_{Ar} – intensity of argon flow, dm^3/min,

W_2^f – final mass of sample determined directly from weighing the sprinkled contents of the crucible, g,

y – number of SiO moles which escaped from reduction system, mole.

REFERENCES

[1] J. Węgrzyn, The influence of intensity of argon flow on therate of mass loss in carbothermal reduction of quartzite to silicon carbide, Metalurgija, 55 (2016), 2, 185-188.

[2] J. Węgrzyn, Mass balance at partial run of quartzite carbothermal reduction, Metalurgija 55 (2016), 2, 209-212.

[3] C. Czosnek, J.F. Janik, Nanopowder silicon carbide and carbon/silicon carbide composites prepared by the aerosol-assisted synthesis, Przemysł Chemiczny 93 (2014), 12, 2020-2024; DOI: dx.medra.org/10.12916/przemchem.2014.2020.

[4] T. Gumuła, S. Błażewicz, Wybrane właściwości cieplne kompozytów C/Si-C-O i C/SiC otrzymanych z prekursorów polimerowych, Kompozyty (Composites) 6 (2006), 1, 68-73.

[5] T. Shimoo, K. Okamura, T. Akizuki, M. Takemura, Preparation of SiC-C composite fibre by carbothermic reduction of silica, Journal of Materials Science 30 (1995), 3387-3394.

[6] Y. Hui-Mei, L. Chang-Wei, Q. Ling-Jun, X. Hua-Qing, X. Tong-Geng and L. Lan, Studies on the thermal stability of nano-SiC powder with excessive free carbon by TG-DTA-MS, XRD and TEM, Journal of Thermal Analysis and Calorimetry, 85 (2006), 3, 657-660; DOI: 10.1007/s10973-006-7647-6.

[7] A. Huczko, M. Szala, A. Dąbrowska, Synteza Spaleniowa Materiałów Nanostrukturalnych, Wydawnictwa Uniwersytetu Warszawskiego, Warszawa, 2012, p. 28.

[8] C. Czosnek, Materiały węglowe modyfikowane nanokrystalicznym węglikiem krzemu SiC, Gospodarka Surowcami Mineralnymi, 23 (2007), 3, 85-91.

[9] PN-EN ISO 21068-2:2010P, Chemical analysis of silicon-carbide-containing raw materials and refractory products, Part 2: Determination of loss on ignition, total carbon, free carbon and silicon carbide, total and free silica and total and free silicon (ISO 21068-2:2008).

[10] Certificate of Certified Reference Material NCS DC 93022 Silicon Carbide, Reissued in 2014, Approved by China National Analysis Center for Iron and Steel (Beijing China).

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