Combined XRD and XRF Technique for the Quantification of the Mass Balance in a Si Carbothermic Production Experiment

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The production of metallurgical grade silicon is based on carbothermic reduction of silica in the submerged arc-furnace. Small scale silicon production experiments have been performed aiming at investigating the kinetics and the reaction mechanisms occurring in the furnace. This paper describes a new combined quantitative technique for the analysis of reaction products from silicon experiments. The method is based on a combination of XRD and XRF techniques and can be used to estimate the total phase mass balance in silicon experiments.

KEY WORDS: silicon; XRD; XRF; phase mass balance.

1. Introduction

Metallurgical grade silicon is produced conventionally by the reduction of silicon dioxide with carbon in a submerged electric arc furnace. In this process, the charge materials, consisting of quartz rock and carbonaceous reducing agents, are charged into the furnace from the top and molten silicon is tapped from the bottom. The system includes many compounds: solid (C, SiC and SiO₂), liquid (Si and SiO₂) and gaseous phases (CO, SiO) are copresent. The reactions take place under atmospheric pressure in a temperature interval of 1500–2000°C.

The main reactions are:

\begin{align*}
SiO₂(g) + C(s) & \rightarrow SiO(g) + CO(g) \quad (1) \\
SiO₂(g) + 2C(s) & \rightarrow SiC(s) + CO(g) \quad (2) \\
2SiO₂(l) + SiC(s) & \rightarrow 3SiO(g) + CO(g) \quad (3) \\
SiO₂(g) + SiC(s) & \rightarrow 2Si(g) + CO(g) \quad (4) \\
2SiO₂(l) + Si(s) & \rightarrow 2SiO(g) \quad (5)
\end{align*}

In the upper low temperature zone of the furnace, carbon and silica react to SiO and CO according to Eq. (1), and the ascending SiO reacts with C to form SiC according to Eq. (2) or condenses to Si and SiO₂. SiO is produced mainly from the reaction of Si with molten SiO₂ (Eq. (5)) that takes place in the lower and hottest part of the furnace. In the hottest part of the furnace SiO₂ reacts with SiC to form Si, SiO and CO according to Eqs. (3) and (4).

Small scale silicon producing experiments have been performed to simulate an industrial furnace. Because of kinetics and carbon reactivity, the reactions do not go to completion, and nonreacted carbon, quartz and silicon carbide are found together with the reaction products.

A quantification of the reaction products involved in the silicon production experiments allows a study of the reaction mechanisms, the silicon yield and the reaction kinetics. Agarwal and Pal⁴) have calculated a phase mass balance to study the reduction kinetics of pellets made of C carbon black and SiO₂. Combustion analysis of the reacted pellets gives the C and O content of the samples. Oxygen content corresponds to retained silica, while carbon content corresponds to the SiC and retained carbon in the system. Total weight loss measured is attributed to the CO and SiO evolution. The calculated CO amount has been verified against the total CO evolution measured by a gas analyzer. Errors below 10% have been reported. Nagamori et al.⁵) have studied the thermodynamics of the whole Si–C–O system theoretically. A mass balance is established before and after the reactions. The number of moles before and after the reaction are interrelated by the Si–O–C element balance and one equilibrium reaction. Nagamori based his quantification on thermodynamic assumptions. Agarwal and Pal based their quantification on measured values, but the analysis method presents several disadvantages: it requires a CO analyzer, it does not distinguish between different SiC polytypes and does not distinguish between C in SiC and elemental C.

Mineralogy and geological applications often use a combination of XRD and XRF analysis techniques to identify phase and elemental composition of rocks.⁶) This method alone is not able to quantify the output phases of a silicon production experiment. The reacted charge contains amorphous silica that can not be quantified by XRD and graphite that can not be quantified by XRF.

The aim of this study is to quantify, without thermodynamic assumptions, the products of different reactions occurring simultaneously in a silicon production experiment. The method combines XRD, XRF with elemental Si, C, O mass balances. The reaction products of a series of small scale silicon producing experiments have been stud-
ied. The method can be used to quantify different SiC polytypes, C, Si, amorphous SiO₂ reaction products as well as SiO and CO lost.

2. Materials and Methods

2.1. Materials and Experimental Procedures

The charged material was in the form of lumps or pellets. Two high-purity hydrothermal quartzes, denoted quartzA and quartzB, one source of high-purity SiC and high purity graphite crucibles have been used. The experimental set-up is shown in Fig. 1. The SiC was a mixture of hexagonal (6H:SiC) and tetragonal (15R:SiC) polytypes, no crystallographic cubic SiC (3C:SiC) was present. The number indicates the number of layers in the stacking sequence, and the letter the class: H, R, C stands for hexagonal, rhombohedral and cubic respectively. According to another designation, hexagonal and rhombohedral polytypes are denoted as α-type, while cubic polytype as β-type. The total weight of the charge was 25 g when pellets were used and 18 g for the case of lumpy charge. The lumps size was 3−5 mm and the pellets had a diameter of 1−2 mm. Pellets consisted of a mixture of quartz and silicon carbide milled to powder (quartz up to 20 μm and SiC up to 10 μm size). Particle size was chosen according to the work done by Agarwal and Pal. Water was used as binder during the pelletizing process. The charge was dried in a graphite crucible at 80 °C for 60 min.

The experiments lasted 80 min. The charge was first heated to 1 800 °C at a heating rate of 90 °C/min, then from 1 800 °C to 2 000 °C at 5 °C/min, and then the temperature was maintained at 2 000 °C for 20 min. The sample was subsequently rapidly cooled at a rate of 100 °C/min.

Two SiO₂:SiC molar ratios have been considered. A molar ratio 1:2 refers to the stoichiometry of reactions (3) and (4). The molar ratio SiO₂:SiC = 1:1 refers to the stoichiometric overall reaction taking place in the inner zone as proposed by Schei and Müller.

The experiments were designed to study 3 factors in eight runs. The eight run design was constructed with a full factor standard table of signs (see Table 1) for two quartz types, SiO₂:SiC molar ratios and charge type. Each run was repeated three times when lumps were used and two times when pellets were used. The experiments with pellets were repeated only twice, because they showed little variability in the weight loss. Representative samples that showed weight losses closer to the average value for each experimental condition were analyzed quantitatively. Solid phases remaining after the experiments were solid reaction products and solid unreacted charge. In particular the solid phases consisted of Si, C, amorphous SiO₂, and different SiC polytypes.

2.2. Method for Analysis

XRD and XRF quantitative analysis X-ray powder diffraction (XRD) and X-ray fluorescence spectroscopy (XRF) are highly complementary materials analysis methods which, when combined, allow phase identification and quantitative analysis. XRF provides highly accurate information about the elemental composition of a sample. The instrument used in the present investigation can be used to estimate the weight percentage of the total elemental Si, but does not to detect light elements such as C and O and not give direct phase information. In contrast to XRF, XRD is the most direct and accurate analytical method to identify and determine the amounts of phases in a sample. However, only polymorphs of crystalline phases can be quantified. A qualitative comparison between the two techniques is shown in Table 2. D8 Advance XRD, BRUKER-EVA qualitative, BRUKER-TOPAS quantitative Rietveld and XRF BRUKER S8 Tiger 4 kW X-ray spectrometer have been used for the analysis. XRD analysis requires a few grams of specimens, while XRF needs about 9 g. In order to confirm the representativity of the sampled material, two parallels of each sample were analyzed by XRD.

Sample preparation The crucible and reacted charge were crushed to a fine powder by means of a tungsten carbide vibratory disc mill. The particle range size was 200 nm−50 μm, which is consistent with XRD and XRF requirements. Particles larger than 50 μm lead to poor statistics and preferred orientation effects. Overcrushed material has highly distorted structure and limited number of crystal planes which lead to a broadening and eventually disappearance of the XRD peaks. Different crushing times combined with particle size analyses have been tested. The optimum crushing procedure consisted of crushing the sample for 5 minutes, sieving the powder obtained at 50 μm, and crushing the

| phase | XRD | XRF |
|-------|-----|-----|
| SiC   | Quantification of different SiC polytypes | Quantification of the elemental Si contained in Si, SiC and SiO₂ |
| SiO₂  | Only quantification of crystalline SiO₂ |   |
| Si    | Quantification of silicon phase |   |
| C     | Quantification of carbon phase | Not possible to quantify |

Table 2. Qualitative comparison between XRD and XRF technique.
powder above 50 μm for 10 more minutes. Particle size was measured by Laser Scattering (LS) Particle Size Analyzer. The cumulative distribution curve is shown in Fig. 2. Since the sample is a mixture of different solid phases (SiC, SiO2, Si and C) and each phase has different specific weight, the volume distribution curve does not coincide with the weight distribution curve.

Calculation of total mass balance The purpose is to identify and quantify the reaction products and unreacted charge of silicon carbothermic production experiments. The unreacted charge consists of SiO2, SiC and C phase. The reaction products consist of Si, SiC, CO(g), SiO(g). Input components are SiO2, SiC charge materials and C from the graphite crucible. The graphite is included in the mass balance, because the crucible reacts with SiO(g) and a thin layer of SiC is formed according to reactions (1), (2). In particular since the experiments are carried out between 1400°C and 2000°C cubic SiC (3C:SiC) is formed.8,10,11) The absence of cubic silicon carbide in the input charge represents a great help for the solution of the mass balance. In this way it is possible to distinguish the SiC consumed in the charge from the SiC formed during the reaction between the crucible and the SiO(g). The amount of reactants is known, while the amount of unreacted charge and reactants products is unknown. The overall output-phase mass balance is written and the amount of nonreacted crucible. From this information, and from the additional information of total weight losses, the amount of CO(g) can be estimated (Eq. (11)). Now the oxygen mass balance can be written and the amount of nonreacted carbon is estimated.

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Weighing of the nonreacted silica, quantification of the graphite by Carbon Leco and observations of backscattering images of the reacted charge, have been used to estimate the error of the method.

$$z = a + b + c - \frac{\text{totSi}}{28.086} \quad (10)$$

$$x = \frac{\text{weightlosses} - z \cdot 44.085}{28.01} \quad (11)$$

$$g = \frac{a - (x + 2)}{2} \quad (12)$$

$$p = \frac{40 \cdot (a + b + c - z - g)}{\frac{\text{SiC}}{\text{Si}}} - 28.086 + 40.097 \quad (13)$$

$$s + t + u = a + b + c - (g + z + p) \quad (14)$$

3. Results and Discussion

The total mass fraction for the eight experiments is shown in Fig. 3. Only the fraction of graphite that has reacted to form SiC is shown as carbon input.

Figure 4 is an example of a XRD spectrum of the reacted charge. The green curve represents the spectrum, the blue curve represents the phase theoretical peaks. The two curves are almost overlapping, and the deviation between them is the error represented by the red curve. Negative and positive deviation peaks represent respectively over and under quantitative estimation for that phase. The quantification of Si and SiC phases shows small errors. On the other hand, the graphite phase shows large asymmetric error peaks. In addition, graphite has high X-ray absorption because of its low atomic number and the analysis is probably affected by the matrix effect. Other sources of errors are the presence of a tungsten phase due to the tungsten carbide crusher used for the sample preparation and the presence of amorphous silica that cannot be quantified. Since the error for the Si and SiC phase is low, their ratio is used for the calculation of the mass balance.

The errors in the quantification of the total C and SiO2
phases for the samples “qzA lumps 1:2”, “qzB lumps 1:2”, “qzB pellets 1:2” and “qzA pellets 1:1” have been calculated. The errors have been calculated on the total weight of the reacted crucible, and are nearly the same for the different phases considered.

In the samples “qzA lumps 1:2” and “qzB lumps 1:2”, nonreacted silica was present as small spheres and it was hence easy to detach the silica from the charge and weigh it. The silica was then mixed again into the charge, crushed to μm size particle and the total mass balance calculated. The calculated amount of silica is compared to the weighed value: 0.62 g SiO₂ and 1.81 g SiO₂ have been calculated respectively for “qzA lumps 1:2” and “qzB lumps 1:2” while 1 g SiO₂ and 2.6 g SiO₂ have been measured respectively for “qzA lumps 1:2” and “qzB lumps 1:2”. The error calculated on the total weight of the reacted crucible is +0.57% for the sample “qzA lumps 1:2” and +1.23% for “qzB lumps 1:2”.

In the third case, “qzB pellets 1:2”, the total elemental carbon content in mass% has been measured by the Leco technique and compared with the value estimated from the phase mass balance. The total elemental carbon includes both C and SiC phase. Both Leco Carbon run on RC-412 and Leco Carbon & Sulphur run on a CS-444 have been used. The measurements were performed by Leco Sweden. The errors are +2.79% and –0.81% for Leco C&S and Leco Carbon respectively.

Two experiments “qzA pellets 1:1” with similar weight loss have been made. The first sample was analyzed in EPMA and no silica has been found. The second sample was analyzed quantitatively. The calculated silica content was 1.24 g corresponding to 1.71 mass%.

Calculated and estimated values as well as the errors between them are shown in Table 3. The method is intended to give a realistic quantification of the phases present in a mixture of SiO₂, SiC, Si and C with absolute errors below 3%. The accuracy of the measurement for each phase depends on its relative amount in the mixture, since the error is calculated on the overall weight of the sample.

Table 3. Errors between calculated and estimated values for the phases SiO₂ and C. All the values are mass% of the overall amount of the reacted crucible.

| sample           | qzA lumps 1:2 | qzB lumps 1:2 | qzB pellets 1:2 | qzB pellets 1:1 | qzA pellets 1:1 |
|------------------|---------------|---------------|-----------------|-----------------|-----------------|
| Phase            | SiO₂          | SiO₂          | C               | C               | SiO₂            |
| Calcul. value    | 1.1%          | 2.8%          | 72%             | 74.7%           | 2.3%            |
| Meas. value      | 1.6%          | 4.1%          | 74.5%           | 73.9%           | 0               |
| Technique        | weighing      | weighing      | Leco C&S        | Leco frac. C    | epma            |
| Error            | 0.57%         | 1.2%          | 2.8%            | 0.8%            | 1.7%            |

Fig. 3. a) Reactants (in moles) for each experimental run; b) Reaction products and unreacted reactants (in moles) for each experimental run.

Fig. 4. XRD spectrum of the reacted charge. The main Si, SiC and C peaks are shown. The green curve represents the spectrum of the sample, the blue curve represents the phase theoretical peaks. The red curve is the deviation curve.
4. Conclusion

Conclusions that can be drawn from the work are:

- A quantitative analytical method for the estimation of solid phases co-present in a mixture of SiO$_2$, SiC, Si and C has been proposed.
- The method combines XRD and XRF analyses with elemental mass balances.
- Absolute errors below 3 mass% are reported.
- The method is not based on thermodynamic assumptions.
- The method allows calculation of a total phase mass balance in silicon producing experiments. The method can be used to study the kinetics of reactions.
- The method requires crushing of the sample to μm size.
- The present quantitative analytical technique appears to be a valid method for the comparison of samples made of mixture of phases and a good tool for the study of kinetics and reacted products.

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