Utilization of Waste Graphite for the Sustainable Production of Silicon Carbide

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Abstract: Silicon carbide (SiC) is a great material for high-tech applications due to its unique mechanical, thermal and electrical properties. The Acheson method that is currently used for its production necessitates temperatures between 2000 and 2500 °C, resulting, thus, in a significant environmental footprint. In this work, an innovative approach for the production of SiC at temperatures below 1000 °C is investigated using metallic magnesium to reduce silica and utilizing waste graphite from the industrial production of graphite molds for non-ferrous metallurgy. According to the results, the molar ratios of silica to graphite and magnesium mainly affected the formation of SiC.

Keywords: waste graphite; silicon carbide; Mg thermal reduction; low energy

1. Introduction

Silicon carbide (SiC) is a remarkable synthetic, non-oxide ceramic material that has gained considerable interest during recent decades due to its unique mechanical, thermal, chemical and electrical properties. SiC is one of the hardest known materials with a high mechanical strength, while it has very high thermal and chemical stability, a high melting point and is oxidation resistant. Such properties make this material attractive for a wide range of specific and high-tech applications, including high-temperature electronic devices, semiconductors and cutting and abrasion tools.

Currently, SiC is manufactured using the Acheson method, which takes place in an Acheson graphite electric resistance furnace and is based on the carbothermal reduction of silica, using mainly petroleum coke, but also anthracite coal, etc., as a carbon source. This concerns a solid-state reaction (Equation (1)) that takes place at very high temperatures above 1700 °C [1]. Usually, the carbothermal reduction process involves the heating of raw materials for a long time (30–45 h) at temperatures ranging between 2200 and 3300 °C.

SiO2(s) + 3C(s) → SiC(s) + 2CO(g) (1)

At temperatures below 2500 °C, primary SiC in the form of cubic polymorphic 3C is formed [2]; at temperatures above 2500 °C, the cubic SiC decomposes, and secondary SiC in the hexagonal polymorphic 6H and 4H forms is crystallized in the gaseous phase [2,3]. The extremely high temperature used in the Acheson process and the long processing time result in a significant environmental footprint. In addition, the high energy consumption, in combination with the low efficiency and the necessary crushing and milling of the coarse-gained product [3,4], makes the Acheson process rather uneconomic and non-viable. Therefore, the need for alternative methods to produce SiC with lower energy consumption is imperative.
So far, there are only a few publications about the production of SiC at temperatures lower than those applied in the Acheson method. Most of them refer to the magnesiothermal reduction of silicon oxide, but the recycling of siliceous waste materials in SiC production has also been investigated. Li et al. [5] studied the synthesis of SiC through the carbothermal reduction of quartz in H2/Ar mixtures in a tube furnace. The involvement of H2 in the process as a reducing agent achieved the starting of SiC formation at 1200 °C and its completion at 1400 °C after 270 min. The increase in temperature resulted in the decrease in the process time, which was reduced to 140 min at 1500 °C and at 70 min at 1600 °C. The natural mineral sungite, which is rich in silica and carbon, was also investigated as a raw material for the synthesis of SiC at the temperature range 1500–1600 °C [6]. In this research, sungite was used in different forms, as an aggregate, pellet and powder, of which the powder proved to be the most effective since no further crushing/milling of SiC was necessary. The variability in the sungite chemical composition was mentioned as the most important drawback of the process. The use of magnesium powder in the synthesis of SiC at 800 °C using sucrose as a carbon source resulted in the formation of the pure moissanite-3c phase of SiC with a cubic crystal structure [7]. Nano-structured SiC was also prepared via the solid-state metathesis reaction of various silica sources, magnesium and carbon [8]. According to this approach, the crystalline b-SiC nanomaterials of varied morphologies were synthesized at 600 °C. Moreover, a single phase of α-SiC with 6H-SiC nanoparticles (from 4 to 20 nm) was successfully synthesized at 750 °C, after 18 h retention time in an Ar atmosphere using metallic Mg as a catalyst [9]. The formation of SiC nanoparticles was confirmed through FTIR, XPS and TEM techniques. Zhao et al. [10] achieved the synthesis of porous nanostructured SiC with a surface area above 300 m²/g at a relatively low temperature of 650 °C via the magnesiothermal reduction of mesoporous silica. According to their experimental results, Mg affected the structure and properties of the final product and seemed to have a dual role in the process, acting as both a reducer and a catalyst.

The synthesis of mesoporous SiC has also been investigated through the recycling of waste materials [11], and more precisely, of e-waste glass and waste rubber tiers as sources of silica and carbon, respectively. The resulting SiC nanofibers presented a large specific surface area (about 70 m²/g) that was affected by the reaction time. The nanoparticles of SiC were also synthesized according to the carbothermic reduction process at 1600 °C using waste printed circuit boards of electronics as both silica and carbon precursors after the pyrolysis of the waste material at 500 °C to decompose the organics to carbon [12]. In addition, the spent pot lining from aluminum electrolysis and carbon gangue was used after the acid-leaching pre-treatment for the synthesis of SiC [13]. According to the results of this research, SiC in a powder form was produced at 1600 °C after 5 h in an inert atmosphere. The recycling of Si wafer cutting sludge as alternative materials in the synthesis of SiC was also investigated [14]. The formation of SiC was achieved through the carbothermic reduction process at 1400–1600 °C, while the mixing ratio of Si-slag to carbon was proved as the most important parameter of the process.

This paper investigates the synthesis of SiC through the magnesiothermal reduction of silica sand utilizing waste graphite from the industrial production of molds for non-ferrous metallurgy as a carbonaceous material. More precisely, this paper presents thermodynamic simulations of the proposed process in the system SiO2-C-Mg using FactSage software, as well as a preliminary experimental study on the basic process parameters that affect the synthesis of SiC. The materials produced were evaluated with the X-ray diffraction method. According to the results, the synthesis of SiC using graphite as a C source is feasible at temperatures below 1000 °C, while the overall process seems to proceed through intermediate reaction steps and product phases.
2. Theoretical Approach

The most frequently proposed reactions for the magnesiothermal reduction of silica to SiC are given in Equations (2)–(4). The thermodynamic equilibrium calculations of the studied system SiO$_2$-C-Mg were based on these reactions.

\[
\begin{align*}
\text{SiO}_2(s) + C(s) + 2\text{Mg}(s) & \rightarrow \text{SiC}(s) + 2\text{MgO}(s) \\
\text{SiO}_2(s) + 2\text{C}(s) + \text{Mg}(s) & \rightarrow \text{SiC}(s) + \text{MgO}(s) + \text{CO}(g) \\
2\text{SiO}_2(s) + 4\text{C}(s) + 2\text{Mg}(s) & \rightarrow 2\text{SiC}(s) + \text{MgO}(s) + \text{C}(s) + \text{CO}_2(g)
\end{align*}
\]

Most researchers consider that the overall reaction of SiC formation in the presence or not of Mg proceeds through intermediate reaction steps. Li et al. [5] accept that SiC is synthesized through the intermediate reaction of SiO (g) formation, which defines the kinetics of the overall reaction. The formation of the magnesium silicide (Mg$_2$Si) and its reaction with carbon was also suggested as an intermediate in the magnesiothermic reduction process to produce SiC [15]. According to this approach, the reaction between Mg$_2$Si and C is a solid-state reaction, taking place on the solid carbon phase.

**Thermodynamics of the SiO$_2$–C–Mg System Reactions**

The thermodynamics of the reactions that take place in the system SiO$_2$–C–Mg towards the formation of SiC were conducted by using the module Equilib of FactSage software and the FactPS, FToxid and FTmisc databases. The module Reaction of Factsage was also used to calculate the standard Gibbs free energy of Reactions (2)–(4).

As shown in Figure 1, the magnesiothermic reaction for the synthesis of SiC according to Equation (2) is thermodynamically favorable even at room temperature since $\Delta G^0$ of the corresponding reaction (Reaction 2) is negative throughout the entire temperature range (Figure 1a). According to Figure 1b, the stoichiometry of Reaction (2) results in the evolution of two phases only, SiC(s) and MgO(s), which are thermodynamically stable up to about 1850 °C. Above this temperature, a gas phase consisting of CO (1 mole), SiO (1 mole) and Mg (2 moles) is formed.

![Figure 1](image-url)

**Figure 1.** (a) Standard Gibbs free energy versus temperature of Reaction (2). (b) Effect of temperature on phase evolution in the system SiO$_2$–C–2Mg based on Reaction (2).

Figures 2 and 3 present the thermodynamic calculations conducted for Reaction (3) and Reaction (4), respectively, according to the reactions stoichiometry. As indicated in Figure 2a, Reaction (3) is spontaneous at above 540 °C. However, the thermodynamic calculations (Figure 2b) revealed that SiC (0.5 mole) was formed at lower temperatures, even from 300 °C up to about 1700 °C, along with of a magnesiosilicate phase named forsterite (Mg$_2$SiO$_4$), while a large amount of C (1.5 moles) remained unreacted in this temperature range. As
shown in Figure 2b, at temperatures higher than about 1850 °C, forsterite decomposed, and the gas phases of CO (1.5 moles), SiO (0.5 mole) and Mg (1 mole) predominated, along with 0.5 mole of SiC crystallized in an alpha phase (α-SiC). The prediction of forsterite formation comprises a strong indication that the magnesiothermic reduction of silicon oxide rather proceeds with intermediate reactions and products.

Figure 2. (a) Standard Gibbs free energy versus temperature of Reaction (3). (b) Effect of temperature on phase evolution in the system SiO$_2$–2C–Mg corresponding to Reaction (3).

Figure 3. (a) Standard Gibbs free energy versus temperature of Reaction (4). (b) Effect of temperature on phase evolution in the system 2SiO$_2$–4C–2Mg对应 Reaction (4).

According to Figure 3b, Reaction (4) occurs with a similar way to Reaction (3); actually this concerns the same reaction, having the same stoichiometry with two-times-higher coefficients of the reactants and double the quantities of the reaction products. However, the standard Gibbs free energy calculations indicated that Reaction (3) is spontaneous at a lower temperature, about 300 °C, which is closer to the prediction of the thermodynamic model calculations (Figure 3b).

3. Materials and Methods

Commercial silica sand (DUROSTIC S.A.) was used in this study. This almost consisted of well-crystallized pure quartz (~90% wt.) with small contributions of aluminum, iron and potassium oxides. Silica sand had a particle size lower than 500 μm, with 90% of its particles larger than 30 μm with a mean particle size about 120 μm. As a carbon source, waste graphite provided by the company CARBONTEC was used; the particle size of waste
graphite was <10 µm. In addition, Mg powder of analytical grade (Alfa Aesar; −325 mesh; 99.8%) was used as a reducing agent.

All the experiments of this study were performed in a muffle lab-scale furnace, operating under an inert atmosphere (Ar gas). For the mixtures of silica sand, waste graphite and Mg powder (Table 1), crucibles of alumina were used. In each test, the crucibles were placed into the furnace, which started operating under Ar gas atmosphere with a heating rate of 10 °C/min to reach a pre-defined temperature. The crucibles were left at this temperature for a pre-defined time, and then the furnace was shut down, and the crucibles were removed after the furnace cooled down. Table 1 summarizes the experimental details of the tests performed in this study.

Table 1. Experimental conditions of the performed tests series (EXP1–EXP3).

<table>
<thead>
<tr>
<th>Tests Series</th>
<th>T (°C)</th>
<th>t (h)</th>
<th>C:SiO₂</th>
<th>Mg:SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>EXP 1</td>
<td>800</td>
<td>3</td>
<td>1:1</td>
<td>1:1</td>
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<tr>
<td></td>
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<td>2:1</td>
<td>2:1</td>
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<td></td>
<td>1:1</td>
<td>1:1</td>
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<tr>
<td>EXP 2</td>
<td>700</td>
<td>6</td>
<td>1:1</td>
<td>2:1</td>
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<td></td>
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<td>2:1</td>
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<td></td>
<td></td>
<td></td>
<td>3:1</td>
<td>2:1</td>
</tr>
<tr>
<td>EXP 3</td>
<td>700</td>
<td>4.5</td>
<td>1:1</td>
<td>2:1</td>
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<td></td>
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The obtained materials were characterized by the X-ray diffraction (XRD) method, using a D8 Bruker diffractometer (CuKα radiation, λ = 1.5418 Å with tungsten filament at 40 kV and 30 mA), in the range 2θ from 2° to 80° with a scanning rate of 2°/min.

4. Results and Discussion

The XRD analysis of the solid materials obtained in this preliminary experimental study revealed that the main products of the magnesiothermic reaction at the studied conditions of temperature and time were MgO, Si and Mg₂Si. The formation of SiC was also detected in the XRD patterns of some solid materials. Furthermore, unreacted SiO₂ was identified in all the obtained materials, indicating the partial completion of the SiC synthesis reaction (Equations (2)–(4)).

According to the experimental results, the molar ratios of C and Mg to SiO₂ in the process mixtures were identified as important parameters, affecting the synthesis of SiC. As shown in Figure 4, the increase in the C-to-SiO₂ molar ratio from 1:1 to 3:1 (excess of waste graphite) clearly promoted the formation of SiC.

Regarding the temperature and time, both of these process parameters did not appear to affect the synthesis of SiC. According to Figure 5, increasing the time by 1.5 hours under the same process temperature (700 °C), as well as increasing the temperature by 100 °C for almost the same process time (3 and 4.5 h) did not obviously affect the intensity of the XRD peaks attributed to SiC. In general, the magnesiothermic reduction of silicon oxide to form SiC is a slow reaction that necessitates more than 18 h for its completion, while the process temperature mainly affects the structure and properties of SiC [7,15].

Considering the effect of Mg, a low Mg-to-SiO₂ molar ratio proved beneficial for the formation of SiC (Figure 6). According to Figure 6, the increase in Mg in the starting mixture enhanced the formation of magnesium silicide (Mg₂Si) instead of SiC, as the latter was not detected in the corresponding XRD pattern. Although a molar ratio of Mg to SiO₂ equal
to five almost duplicated the stoichiometric amount of Mg in all the reactions considered for the magnesiothermic reduction of silicon oxide (Equations (2)–(4)), it was not able to advance the formation of SiC. In opposition, this Mg excess was consumed in the reaction between SiO\textsubscript{2} and Mg to form Mg\textsubscript{2}Si.

![Figure 4](image-url)

**Figure 4.** The XRD patterns of the materials obtained in EXP-2 (700 °C; 6 h) under the different molar ratios of C to SiO\textsubscript{2}, 1:1 (blue line) and 3:1 (red line), and a constant molar ratio of Mg to SiO\textsubscript{2} (2:1).

![Figure 5](image-url)

**Figure 5.** The XRD patterns of the materials obtained under different process times and temperatures and constant molar ratios of C to SiO\textsubscript{2} (1:1) and Mg to SiO\textsubscript{2} (2:1).

Based on the findings of the XRD study presented in Figures 4–6, it seems rather certain that the magnesiothermic reduction of silicon oxide by using waste graphite as a C source proceeds via intermediate reactions and products. In particular, as was suggested in other relevant studies [15,16], Si is formed as an intermediate product of the reaction between SiO\textsubscript{2} and Mg (Equation (5)), which, in turn, reacts with carbon to form SiC, according to the reaction given in Equation (6).

\[
\text{SiO}_2 + 2\text{Mg} \rightarrow 2\text{MgO} + \text{Si} \tag{5}
\]

\[
\text{Si} + \text{C} \rightarrow \text{SiC} \tag{6}
\]
The excess of Mg also favored the formation of Mg₂Si as an intermediate product (Figures 4–6) after the reaction with the residual SiO₂. Mg₂Si reacts then with carbon to form SiC, as described the overall reaction in Equation (7) [15].

\[ \text{SiO}_2(s) + C + 4\text{Mg} \rightarrow \text{Mg}_2\text{Si} + \text{C} + 2\text{MgO} \rightarrow \text{SiC} + 2\text{Mg} + 2\text{MgO} \] (7)

Specifically, the intermediate product Mg₂Si is considered to diffuse into the carbon solid phase, where it reacts by releasing two Mg atoms in the SiC phase that are backward-diffused in the SiO₂ solid phase to continue the process [15]. After the initial reaction phase, the supply of Mg on SiO₂ becomes the rate-limiting step of the overall reaction. It is obvious that the excess of Mg, with a molar ratio of Mg to SiO₂ equal to four or higher, allows for the complete conversion of SiO₂ to Mg₂Si, without needing the Mg back-diffusion process, thus accelerating the reaction of SiC synthesis.

![Figure 6. The XRD patterns of the materials obtained in EXP-3 (700 °C; 4.5 h) under different molar ratios of Mg to SiO₂ (2.5:1 and 5:1) and a constant C-to-SiO₂ molar ratio (2:1).](image)

5. Conclusions

The main conclusions of this study are the following:

1. The sustainable production of silicon carbide by utilizing the waste graphite generated in industrial processes is feasible through a magnesiothermal reduction process that takes place at temperatures below 1000 °C.

2. The thermodynamic study of the system SiO₂-C-Mg confirms the potential of SiC formation at temperatures below 1000 °C.

3. The molar ratios of SiO₂ to C and SiO₂ to Mg proved to be significant parameters of the process.

4. The synthesis of SiC following the magnesiothermal reduction of silicon oxide proceeds via intermediate reaction steps and products, which define the rate of the overall reaction.

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References

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