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Gas transport mechanisms and the behaviour of impurities in the Acheson furnace for the production of silicon carbide

W. R. Matizamhuka*

Vaal University of Technology, Department of Metallurgical Engineering, South Africa

* Corresponding author.

E-mail address: wallace@vut.ac.za (W.R. Matizamhuka).

Abstract

The Acheson process still remains the method of choice for the industrial production of silicon carbide. The furnace operates in an unsteady thermal regime thus making it difficult to determine the kinetics of the process. In the present study, FactSage Software was used to get an insight and verify the dominant reactions occurring during operation. Moreover, the effect of impurities on the overall process efficiency and product quality is also discussed. The study is intended to clarify the effect of varying the SiO_2/C ratio on the composition of the reactants taking part in the SiC formation reaction. Further, a deeper understanding of the formation process is developed and verified.

Keywords: Materials science, Industrial engineering, Physical chemistry

1. Introduction

Silicon carbide (SiC) has gained industrial importance over the years owing to its attractive properties such as low density, good creep resistance, high hardness and wear resistance, high temperature stability, high thermal conductivity and high elastic modulus and strength. A large portion of SiC produced in South Africa is medium grade (82–88%SiC) and therefore is extensively used as a

reductant and deoxidant in the iron and steel making industry [1, 2]. The bulk of SiC world production still comes from the decades old Acheson Process. The process essentially involves the high temperature (in excess of 2000 °C) reduction of quartz with a suitable carbon source (such as petroleum coke, coal, anthracite, charcoal) in an electrically heated resistance furnace [3].

The furnace construction consists of a central electrode in the form of a graphite core surrounded by a mixture of raw materials consisting of mainly a carbon source, silica sand and in some instances additives such as sawdust and sodium chloride (NaCl) are included [4, 5, 6, 7]. In the pioneering work, the sawdust was used to improve gas permeability which in turn enhances the gas-solid reaction kinetics [4, 5, 6, 7]. The NaCl was mainly added to get rid of impurities such as Al_2O_3 , Fe_2O_3 , MgO and CaO in the form of gaseous chlorides [4, 5, 6, 7]. This practice is however not very common in present day operations owing to the hazardous nature of the gaseous chlorides produced during operation. Moreover, this practice was proved to be ineffective for the purification process [6]. The trend nowadays is aimed at harnessing the energy in the gaseous products [7]. It must be noted however that the Acheson Process is an energy intensive process requiring significant power consumption of the order 7300–7600 kWh/t of product [4, 8, 9]. This coupled with low commercial yields of ~15–19% has effectively pushed the SiC producers, especially in the developing world, to abandon the use of costly high purity raw materials and rather opting for readily available low-purity raw materials, such as coal to reduce the cost of production [2, 9].

However due to the existence of a variety of impurities in coal, it would be of interest to understand the behaviour of some of the most prominent impurities found in coal and their impact on the process efficiency and the quality of SiC produced. The formation of SiC is dominated by gas/solid sub reactions at temperatures in excess of 2000 °C. The issue of gas transport mechanisms has not been properly addressed in earlier literature and there is controversy over the role of the liquid product, SiO in the formation of SiC. The thermodynamics of SiC formation has been covered quite extensively in earlier studies [10]. In 2009, Zhou and Telle carried out a thermodynamic study on the purification mechanism in the Acheson Process using FACTSage Software [6]. The study addressed the previously held misconception that NaCl enhances the purification process. Since then, no follow up study has been carried out to verify this misconception using FACTSageTM. Moreover, the effect of varying the SiO₂/C ratio on the gas composition was not addressed in previous studies. Thus this study is aimed at developing a deeper understanding of the SiC formation process and the effect the raw material ratio may have on the process efficiency and yield.

2. Methodology

The FACTSage™ 5.4.1 Thermodynamic Software and the FACT databases were used for calculations and graphical plots. An iterative approach was used to assess the behaviour of products at varying temperature conditions to validate the use of FACTSage™ 5.4.1 under dynamic conditions. The study was done under a temperature range of 1500–2500 °C which adequately covers the temperature regime for SiC formation. To clarify the composition of gas phase, calculations were carried out using FACT Software. For the interpretation of the compositions it is useful to take into account Gibbs phase rule. The degree of freedom, F depends on the number of components, C (in Si-C-O = 3) and the number of phases P in the following way; $F = C + 2 - P = 5 - P$ thus a maximum of 5 phases can be in equilibrium at a certain temperature and pressure. The pressure in the calculations and in the furnace was fixed, thus this would correspond to one degree of freedom, the temperature. This implies that in the presence of 3 phases (2 solids and 1 gas) the composition of the gas phase is fixed and does not depend on the ratio of the components provided the same solid phases are formed. The results were compared to existing literature findings to draw conclusions and fill some of the existing gaps left out in earlier findings. The behaviour of impurities was predicted over the SiC formation temperature range (1500–2500 °C). The main cationic impurities of the raw materials Al, Fe, Ca, Mg, and alkaline metals were considered in the modelling of impurity behaviour.

2.1. Background

There are different models in open literature that describe the thermodynamic and kinetics of the Acheson process. In the literature before 1970 mostly only simple reactions were taken into account and not a complete minimisation of free energy was used for the explanation of the process [11, 12, 13]. In the 1980s the formation of liquid/solid SiO was proposed to describe the behaviour of the system [10]. There exist no reliable proof of the existence of such a compound. Therefore, the new databases do not contain such compounds [14]. In Fig. 1 below the calculated phase diagram of SiO₂-C is shown. The formation of SiC is favourable above 1515 °C. In the presence of excess C (>3 mol C per mol SiO₂) SiC and C are formed. Below the stoichiometric composition SiC forms in a mixture with SiO₂ and gaseous products at temperatures between 1515–1800 °C and at temperatures >1800 °C only gaseous products are more prevalent. The gaseous products formed are a function of the mole ratio between SiO₂ and C raw materials. The specific gaseous products formed are found in section 3.0. However, above a SiO₂/(SiO₂+C) mole ratio of >0.5 and temperatures in excess of 1800 °C no SiC forms. This phase diagram differs from the one by Nagamori *et al* in the SiO₂ rich area due to the difference in the stability of SiO phase mentioned earlier.

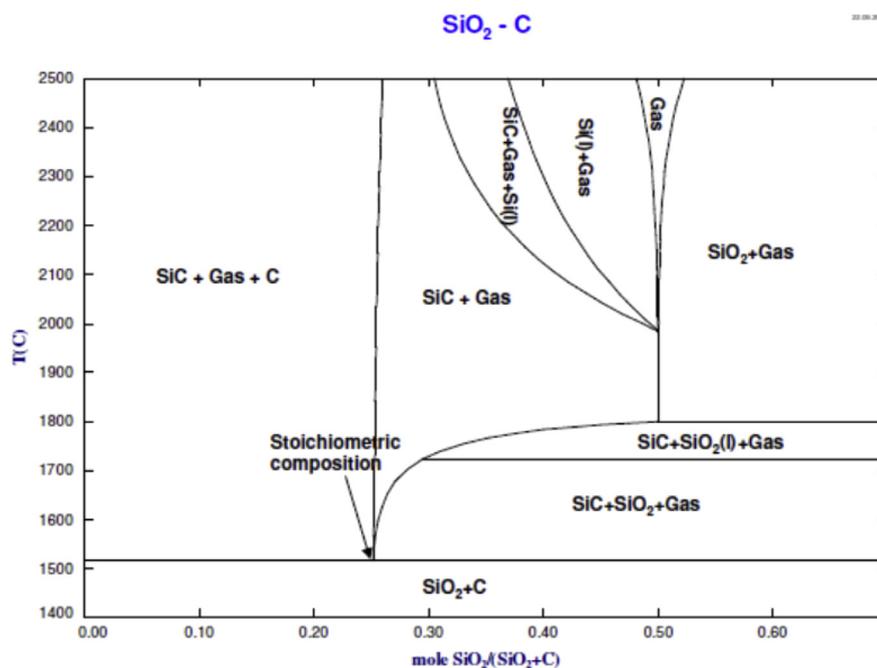


Fig. 1. Calculated SiO₂- C phase diagram (FACTTM Software).

In open literature, the generally accepted mechanism of SiC formation is through the gas/solid interactions which involves the SiO gaseous species as shown in reactions (1), (2) and (3) below.



and for the SiC formation:



To further elaborate on this, a simple model was developed to give an insight on the reactions occurring at the particle surfaces as follows:

The reaction in Fig. 2 is dominated by water evaporation and release of volatiles. Oxygen in air and water start to react with C to form a CO₂/CO/H₂ atmosphere at temperatures >700 °C. Further reaction of CO₂ to form CO (Boudouard reaction) result in a highly reducing atmosphere.

The reaction in Fig. 3 is dominated by the reduction of SiO₂ through possible solid-gas and solid-solid (depends on C reactivity) reactions. Formation of SiC layers on C surface initiate at temperatures 1515–1530 °C. Thickening of SiC layers restrict further reaction due to formation of a diffusion barrier. Generally acceptable crystal

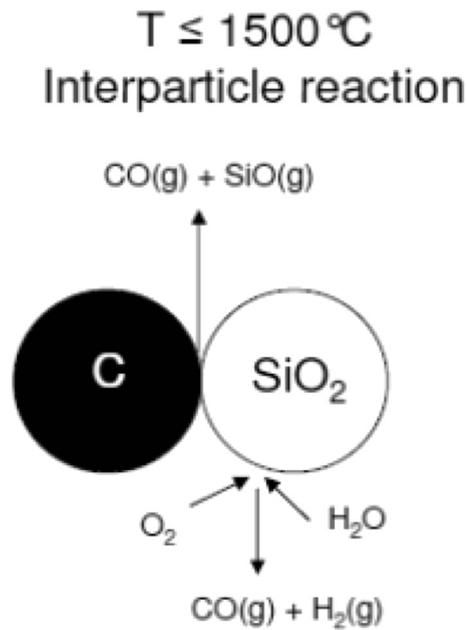


Fig. 2. Interparticle reaction in the initial stage at $T \leq 1500\text{ }^{\circ}\text{C}$.

growth mechanism is the shrinking core model which is both diffusion and phase boundary controlled.

At temperatures below SiO_2 fusion point ($<1727\text{ }^{\circ}\text{C}$) SiC formation through solid-solid reactions is limited due to low diffusivity (Fig. 4). At temperatures $1727\text{ }^{\circ}\text{C}$, SiO_2 melts and contacts the solid C leading to surface reactions. In areas with local carbon deficit, $\text{Si}(l)$ and $\text{Si}(g)$ are likely to form and can lead to SiC formation by direct contact with C . At temperatures in excess of $2000\text{ }^{\circ}\text{C}$, SiO_2 is completely consumed leading to SiC formation.

It must be noted that the decomposition of SiO_2 at temperatures in excess of $2000\text{ }^{\circ}\text{C}$ may lead to increased gaseous product formation near the furnace core and the

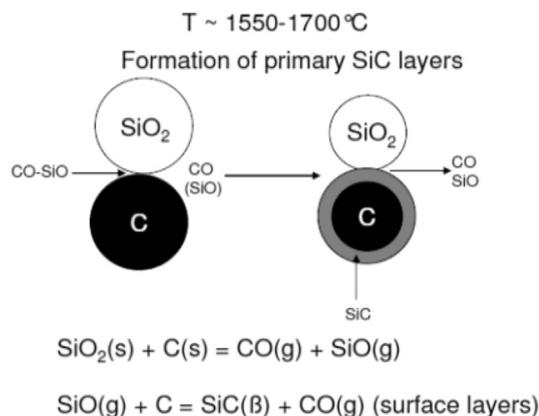


Fig. 3. Summary of the initiating the reaction ($T: 1550\text{--}1700\text{ }^{\circ}\text{C}$).

T > 1750 – 2000 °C
 Melting of SiO₂ and breaking of surface SiC layers

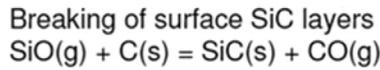
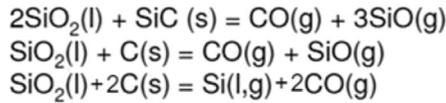
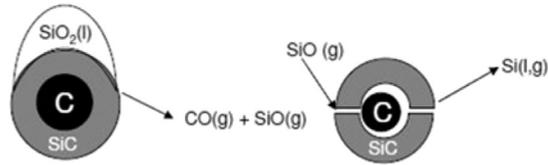


Fig. 4. Reaction acceleration stage ($T > 1750\text{--}2000\text{ }^\circ\text{C}$).

migration of these products towards the cooler outer regions. The ease of migration (level of porosity initially of raw materials SiO₂ and C and later including that of the formed SiC) and extent of reaction of the gaseous products that take part in the SiC formation process have a direct impact on the yield obtained.

3. Results and discussion

Fig. 5 below shows the calculated gas phase composition over the stoichiometric mixture of SiO₂ and C for the overall pressure of 1 atm and 0.5 atm in the

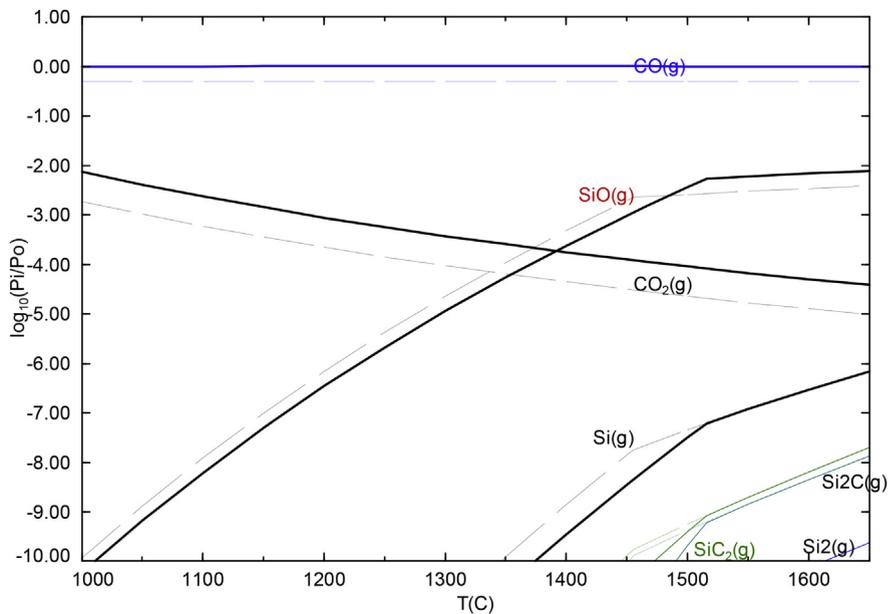


Fig. 5. Composition of the gas phase over SiO₂/C (stoichiometric composition mol ratio 1:3) in CO atmosphere (dashed lines pressure 0.5 bar, solid lines 1 bar).

temperature range 1000–1600 °C. Fig. 2 gives only species with a partial pressure of $>10^{-10}$ bar.

The calculations were extended over a higher temperature range (1600–2400 °C) with the stoichiometric SiO_2/C mol ratio of 1:3 respectively. This data is presented in Fig. 6 below.

A further calculation was carried out to show the effect of varying the SiO_2/C mol ratio on the gas composition (Fig. 7) in the temperature range 1600–2400 °C. Only the dominant gaseous products were taken into consideration.

Thermodynamic calculations show that several gaseous products exist. The gaseous species identified in the calculated plots above are Si, CO_2 , Si_2C , Si_2O_2 , Si_2 , CO and SiO. A comparison of the partial pressures of these gaseous products show that CO and SiO are the dominant components and the partial pressures of the other gaseous products are relatively very low to take part in the SiC formation reaction.

Fig. 8 gives the vapour pressures over the stoichiometric composition of $\text{SiO}_2/3\text{C}$ and 1mol% of CaO and MgO calculated against the amount of SiO_2 . The data shows that MgO and CaO evaporate as Mg (g) and Ca (g). Mg completely evaporates at lower temperatures (1600 °C) in comparison to Ca (1850 °C). CaO and MgO stabilize on the other hand as silicates. Whereas pure SiO_2 completely converts to SiC at 1515–1600 °C the Ca and Mg silicates are stable up to 1850–1900 °C.

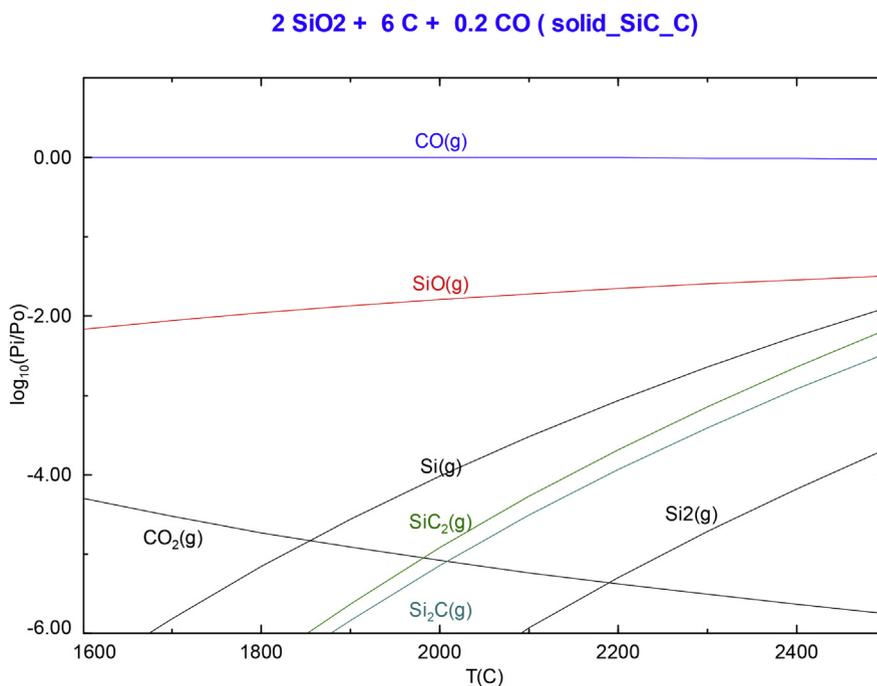


Fig. 6. Composition of the gas phase over SiO_2/C for a SiO_2/C mol ratio 1: 3 (solid phases SiC + C).

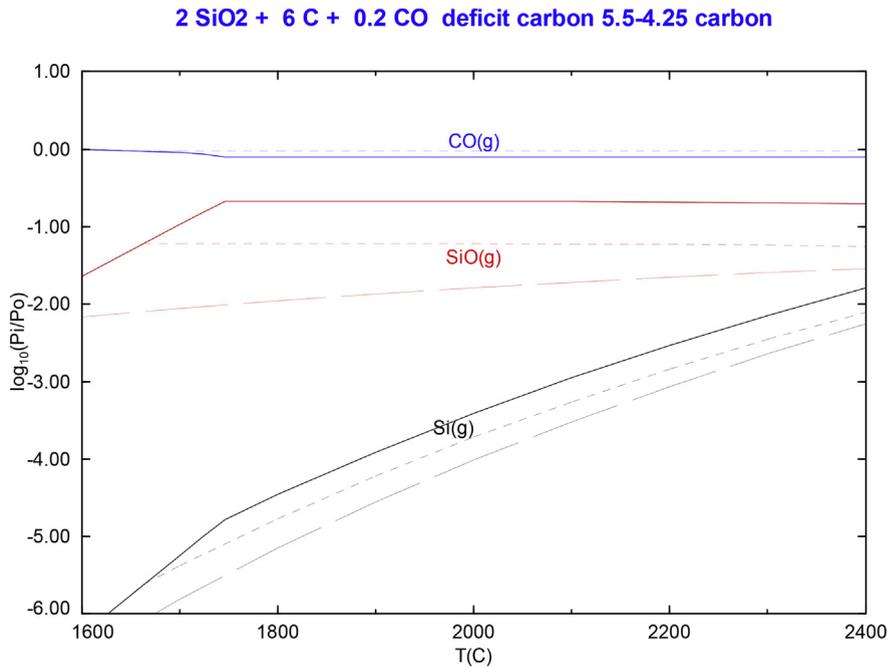


Fig. 7. Partial pressure of CO, SiO and Si as a function of the SiO₂/Carbon mol ratio (— 1:2,125; - - - 1:2,75; - · - 1:3).

The behaviour of alumina is shown in the calculated vapour pressures over the stoichiometric composition of SiO₂/3C and 2.5mol% of Al₂O₃ calculated against the amount of SiO₂ (Fig. 9).

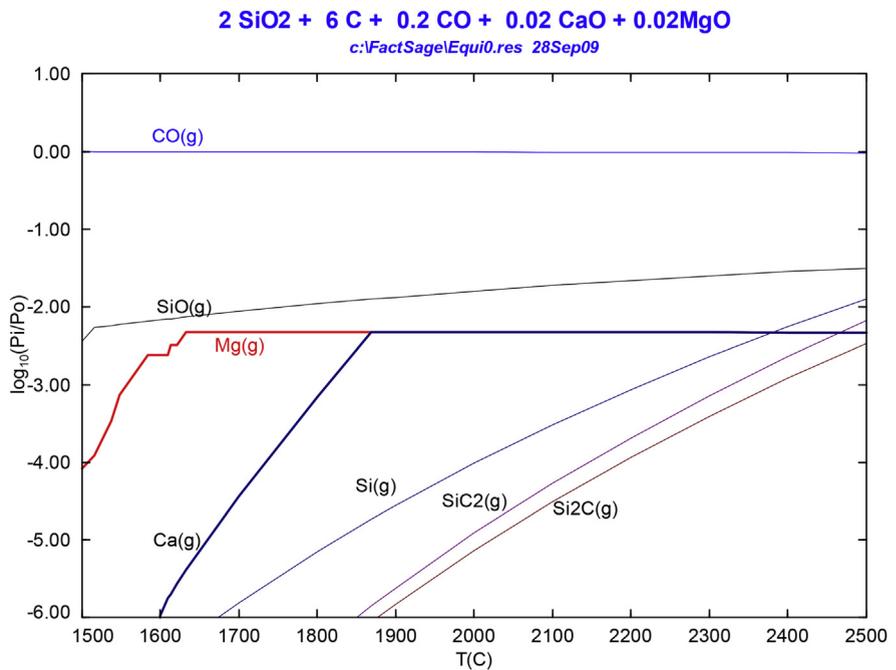


Fig. 8. Calculated vapour pressure over the stoichiometric composition of SiO₂/3C and 1 mol % of CaO and MgO (calculated against the amount of SiO₂).

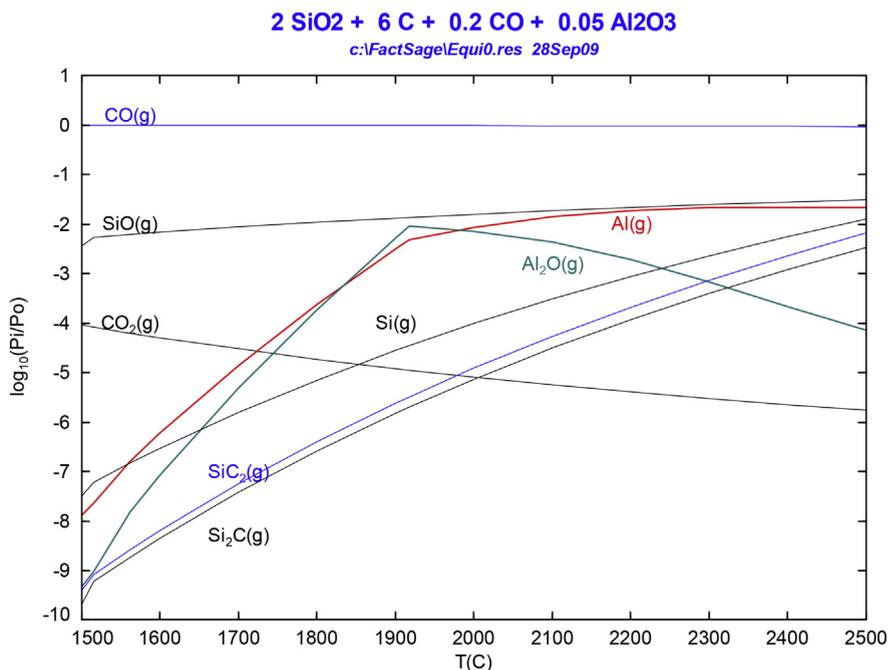


Fig. 9. Calculated vapour pressures over the stoichiometric composition of SiO₂/3C and 2.5 mol % Al₂O₃ (calculated on the amount of SiO₂) as function of temperature.

Alumina is stable up to 1900 °C, nevertheless Al₂O₃ reacts in a wide temperature range with carbon forming gaseous Al₂O and Al as summarised by reactions (4) and (5);



The partial pressures increase strongly with increasing temperature up to the complete decomposition of Al₂O₃, at approximately 1900 °C (see Fig. 9). At higher temperatures (in excess of 1900 °C) the Al pressure increases whereas the Al₂O equilibrium pressure reduces. This sudden increase in Al(g) pressure can be a result of the reduction of Al₂O (g) at these temperatures.

The FeO reduces at lower temperatures ~ 1500 °C and the partial pressure of Fe increases at higher temperatures (Fig. 10). The iron stabilizes the Si which can be locally formed. At 2300–2400 °C the gas pressure of gaseous Fe reaches nearly that of SiO. Therefore it is likely to be transported out of the reaction zone due to the temperature gradient. The amount transported strongly depends on the overall amount of gas.

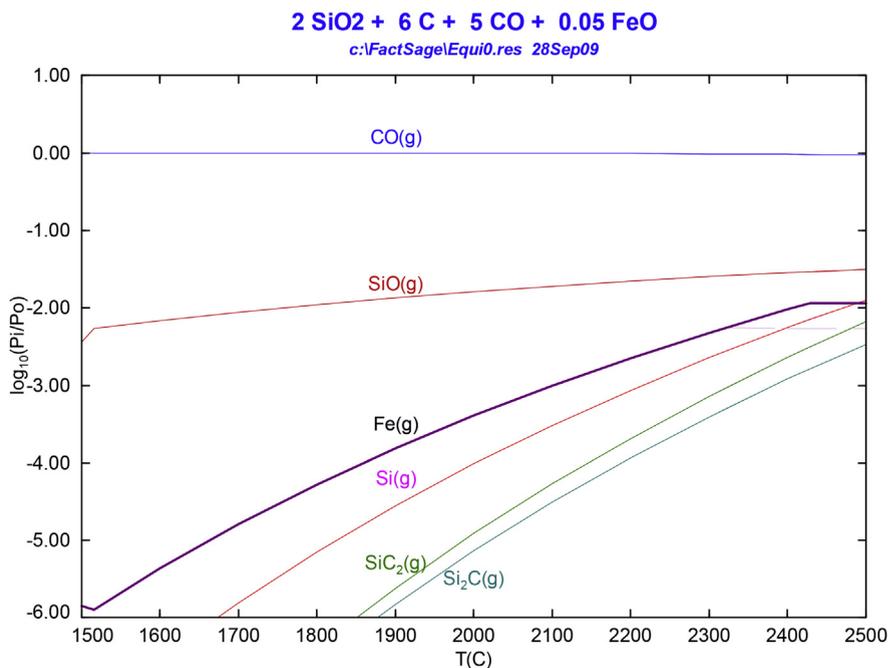


Fig. 10. Calculated vapour pressures over the stoichiometric composition of SiO₂/3C and 2.5 mol % FeO (calculated on the amount of SiO₂) as function of temperature with different amount of gas phase.

4. Conclusion

The calculations have reconfirmed that the formation of Silicon Carbide in the Acheson process is dominated by solid-gas reactions. The dominant gas phases taking part in the process are SiO and CO. The CO formed is more stable in the hotter zone whereas other gas components are more stable in the cooler regions. CO is the major component of the gas atmosphere. The temperature at which the SiC is formed in a CO atmosphere is strongly depended on the gas pressure. A high CO partial pressure enables the reaction between CO and SiC to produce SiO required for the formation of new SiC crystals. The existence of a liquid phase SiO suggested in earlier studies is not substantiated in the present study.

The impurities CaO and MgO have been shown to evaporate as Ca(g) and Mg(g) at temperatures below 2000 °C. These tend to enrich in the outer zone of the furnace and these impurities are least expected in the inner core zone. Alumina undergoes a reduction reaction to form gaseous Al and Al₂O in a wide temperature range. The alumina decomposes at temperatures above 1900 °C. The study has shown that the partial pressures of gaseous Al and Al₂O increase rapidly up to 1900 °C. Thus Al is mostly expected to be a common contaminant in the reaction zone. Iron oxides can be reduced at low temperatures ~ 1500 °C and can form stable silicides which remain in the high temperature zone. Furthermore, gaseous Fe is very stable at high temperatures and is bound to remain as a common contaminant.

A SiO₂:C ratio of 1:3 is recommended with a slight excess amount of C to maximise the chances of large quantities of gaseous products (SiO and CO) formation and high SiC yields. Furthermore, it is feasible to use raw materials containing CaO, MgO and Fe₂O₃ as impurities (low quality carbon sources such as coal) since most of these impurities decompose at the operating temperatures.

Declarations

Author contribution statement

W. R. Matizamhuka: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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