

THERMODYNAMICAL MODELING OF SILICON CARBIDE SYNTHESIS IN THERMAL PLASMA

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Abstract

The synthesis process of solid SiC in thermal plasma was investigated theoretically by computing the equilibrium composition of the gas mixtures involving silicon and carbon in the presence of argon and hydrogen at various silicon/carbon amounts and at two different total pressures in the system, in the temperature range between 1000 and 6000 K. Use is made of the fact that a thermal plasma, by definition, is a plasma in (local) thermodynamical equilibrium, which makes possible the theoretical determination of its equilibrium composition at definite temperature by employing Gibbs free energy data for the compounds present in the system. From the calculated compositions of the investigated gas systems the temperature-composition phase diagrams were obtained. Using these data the temperature zones with saturated and/or oversaturated vapour of SiC as well as of Si and C were determined and the possibility of the formation of SiC in the solid state via different reaction routes was analyzed.

Keywords: SiC synthesis, thermal plasma, thermodynamics of SiC

Introduction

Silicon carbide (SiC) is a mineral that was first discovered in fragments of the meteorite found at Diablo Canyon in Arizona. It was named Moissanite in honor to its discoverer Nobel Prize winner Henry Moissan. Silicon carbide does not occur naturally; it is produced by high temperature chemical reactions. Commercially, SiC is produced in Acheson furnace [1, 2] where a mixture of high-quality sand and low-sulphur petroleum coke with addition of common salt and sawdust is packed around a graphite core. The mixture is then heated to reach a maximum temperature of approximately 2700°C, after which the temperature is gradually lowered. SiC particles produced in this process are large agglomerates with a wide range of particle sizes. The sintered or hot pressed parts of SiC are usually porous.

Two solid phases of SiC, SiC (β) (cubic 3C diamond-like structure) and SiC (α) (hexagonal) are known but intermediate between cubic and hexagonal are also found in the various polytypes of SiC. Silicon carbide is a very hard material, at Mohs hardness

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scale 9.25 (diamond is 10), and high refractive, with index of refraction of 2.6–2.7 (diamond's index is slightly lower, 2.42); it has high thermal conductivity ($\sim 5 \text{ W cm}^{-1} \text{ K}^{-1}$) and is chemically resistant. As semiconductor, that can be operated at temperatures higher than 600°C (silicon devices are limited to operation temperature below 300°C), and in chemically hostile environments, SiC is material of choice for high temperature, high voltage and high frequency applications. Because of these characteristics, different modern techniques have been applied for the synthesis of silicon carbide, for example Chemical Vapour Deposition (CVD) method, where the precursors used for growth of SiC (usually silicon and propane), transported by a carrier gas to a hot zone and decomposed into atoms and radicals, diffuse down onto a (cooled) substrate, producing epitaxial film of SiC [3]. Molecular beam epitaxy [4] method has also been applied to obtain silicon carbide. A very promising method for the synthesis of the high purity ultra-fine powder (in size range 10–100 nm) of silicon carbide is thermal plasma method [5–7]. Reactants as elemental silicon with methane as a source of carbon, are introduced into Ar/H₂ (thermal) plasma [7]; They evaporate and depending on temperature partially dissociate into atoms and ionize producing ions and electrons. The formation of molecules and radicals stable at higher temperatures is also possible. In the plasma zones with lower temperatures, or by rapid cooling (quenching) of this system under controlled conditions, saturated or supersaturated vapor is formed, and the formation of ultra-fine (solid) particles can be achieved.

In this paper the synthesis process of solid SiC in thermal plasma is investigated theoretically by computing the equilibrium composition of the gas mixture involving silicon and carbon in the presence of argon and hydrogen at various silicon/carbon amounts, at different ratios of silicon and carbon amounts, and at two different total pressures in the system, in the temperature range between 1000 and 6000 K. Use is made of the fact that a thermal plasma, by definition, is a plasma in (local) thermodynamical equilibrium, which makes possible the theoretical determination of its equilibrium composition at definite temperature by employing Gibbs (free) energy data for the compounds present in the system, and assuming that the equilibrium of the system corresponds to its minimum energy state.

We point out here that thermodynamical calculation can be very useful for understanding the basic processes in particular plasma processing, but they can not explain all the details arising during experiments, because some steps in plasma synthesis are, or can be, far from equilibrium. Additional information about structure modifications of SiC during heating (or cooling), obtained for example from Thermal Analysis experiments [8, 9], are very useful for the optimization of the synthesis process.

Method of calculation of equilibrium composition

Two basic approaches are used to determine the composition of the complex mixtures at high temperatures. In the first one the thermodynamic equilibrium constants for the decomposition and ionization reactions together with the mass conservation law and electrical neutrality are employed to determine equilibrium composition [10]. The second method, based on minimization of the Gibbs free energy, is used in this paper.

The calculation of the equilibrium gas mixture compositions under condition of constant pressure is carried out using the method of White *et al.* [11], extended for the mixtures containing charge particles [12]. It is based on the fact that the equilibrium of the system corresponds to its minimum energy state. The free energy, G , of the system is the sum of the chemical potentials, μ_i , multiplied by the mole fractions, x_i , of its components

$$G = \sum_{i=1}^n x_i \mu_i \quad (1)$$

where n is the number of chemical species and x_i are their mole fractions to be determined. The set of x_i values leading to the equilibrium can be obtained by solving the equation

$$\delta G = 0 \quad (2)$$

at the fulfilled mass balance condition

$$\sum_{i=1}^n a_i x_i = b_j; \quad j=1, 2, \dots, m \quad (3)$$

where m represents the number of elements in the system, a_i is the number of atoms of element j in the molecule i , and b_j is coefficient proportional to the percentage (or mole fraction) of the element j in the system.

The quasineutrality of a system containing also charge species is ensured by the condition

$$\sum_{i=1}^n q_i x_i = 0 \quad (4)$$

where q_i represents the charge of species i .

According to the method of White *et al.*, the mole fractions x_i are calculated by an iterative procedure. One starts with any set of positive numbers x_{i0} which satisfy Eqs (3) and (4) and builds the zeroth-order approximation for G . The free energy is then expanded into a Taylor series up to the quadratic terms in $x_i - x_{i0}$. The conditions (3) and (4) are taken into account with help of Lagrange multipliers π_j . A minimization of the free energy leads to a system of linear equations which determine the improved values for x_i and thus a new approximation for G . The procedure is repeated until convergence is achieved. It should be noticed that the dimension of the system is $(m+1)$, i.e. it depends only on the number of the elements in the system (i.e. not on the number of chemical species considered). The concentrations of the species in traces can be calculated using the equation:

$$z_i = \exp \left[- (G/RT)_i - \ln p + \sum_i a_i \pi_j \right] \quad (5)$$

where p , T , R are total pressure in the system, temperature and gas constant, respectively.

Table 1 Species considered in the calculation

C	C ₂	C ₃	C ₄	C ₅	C ⁺	C ⁻	H ₂	H ₂ ⁺	H	H ⁺
H ⁻	CH	CH ₂	CH ₃	CH ₄	CH ⁺	C ₂ H	C ₂ H ₂	C ₂ H ₄	C ₂ H ₃	C ₂ H ₅
C ₂ H ₆	C ₂ ⁻	C ₂ ⁻	e	C ₃ H	C ₄ H	C ₅ H	C ₆ H	C ₆	C ₃ H ₂	C ₄ H ₂
C ₃ H ₂	C ₆ H ₂	C ₃ H ₃	C ₄ H ₃	C ₅ H ₃	C ₆ H ₃	C ₃ H ₄ ¹	C ₃ H ₄	C ₅ H ₄	C ₅ H ₄	C ₅ H ₄
C ₆ H ₄	C ₆ H ₄	C ₆ H ₄	C ₃ H ₅	C ₄ H ₅	C ₄ H ₅	C ₃ H ₆	C ₃ H ₆	C ₄ H ₄	C ₄ H ₄	C ₄ H ₆
C ₄ H ₆	C ₄ H ₆	C ₄ H ₆	C ₅ H ₆	C ₆ H ₆	C ₃ H ₈	C ₄ H ₈	C ₄ H ₈	C ₄ H ₈	C ₄ H ₈	C ₄ H ₈
C ₄ H ₁₀	Si	Si ⁺	Si ₂	Si ₃	SiC	Si ₂ C	SiH ₄	SiH	Ar	Ar ⁺

¹The same stoichiometric formulae repeated means different isomer

The compositions of Ar/H/C/Si gas systems were calculated in the temperature range between 1000 and 6000 K, at total pressures of 1 and 0.25 bar and at Si:C ratios of 1, 2 and 0.2. Mole fractions of Si (C) [b_j from Eq. (3)] were varied, and the mole fraction of hydrogen was taken as constant (0.08). These gas mixtures were considered as single phase systems. The mole ratios chosen should simulate argon plasma with hydrogen in presence of silicon and carbon. As mentioned before, this plasma is usually obtained introducing the gas mixture of hydrogen with small amount (1–3%) of some hydrocarbon, for example CH₄, into the main plasma gas, argon. Silicon is injected in the form of powder into the plasma.

Since the reliability of the calculation depends on the number of species taken into consideration, we consider as many as 77 species (atoms, ions, molecules, molecular ions, radicals), Table 1, that could be formed under (thermal) plasma conditions, and whose Gibbs (free) energy data were available [13]. It was, however, shown that the hydrocarbons with larger number of hydrogen and carbon atoms insignificantly contributed to the plasma composition at temperatures higher than 2000 K.

Results and calculations

The equilibrium composition of Ar/C/H/Si gas mixture presented in Figs 1, 2, 3 and 4 relates to the particular mixture that consists of mole fractions 0.0008 of Si, 0.0008 of C (Si:C=1:1), 0.08 of H, and 0.9184 of Ar at the total pressure of 1 bar. The equilibrium partial pressures of hydrocarbons, hydrogen or carbon containing species, as function of temperature, are shown in Figs 1 and 2. From the results presented in Figs 1 and 2 it can be seen that at temperature below 2000 K hydrogen is present in the plasma in the form of molecular hydrogen (H₂). At these temperatures carbon is mostly present in the form of CH₄ and C₂H₂ molecules. At temperatures between 1500 and 3500 K the C₂H₂ molecule is of the highest partial pressure among hydrocarbons; its partial pressure is almost constant in this temperature range. At higher temperatures (3500–6000 K) the dominant carbon-containing form (with respect to its concentration in the plasma) is atomic carbon, followed by smaller amounts of

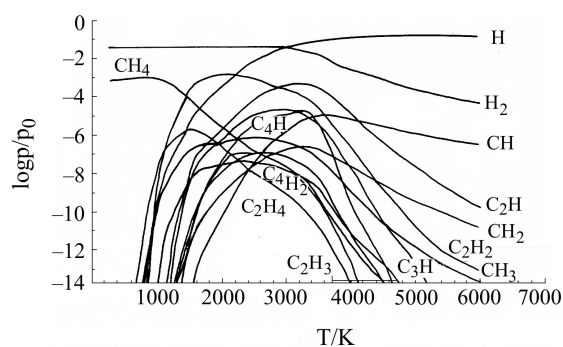


Fig. 1 Equilibrium partial pressures of hydrocarbons and hydrogen containing species in Ar/C/H/Si gas system, as function of temperature; C, Si = $8 \cdot 10^{-4}$, H = 0.08, $p = 1$ bar

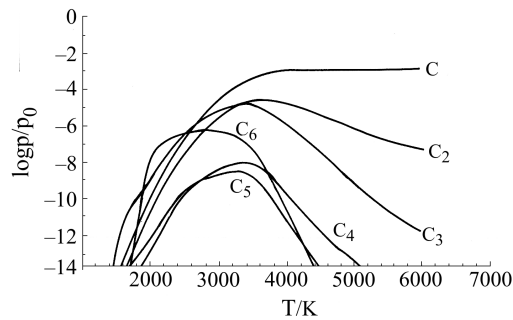


Fig. 2 Equilibrium partial pressures of carbon containing species in Ar/C/H/Si gas system, as function of temperature; C, Si = $8 \cdot 10^{-4}$, H = 0.08, $p = 1$ bar

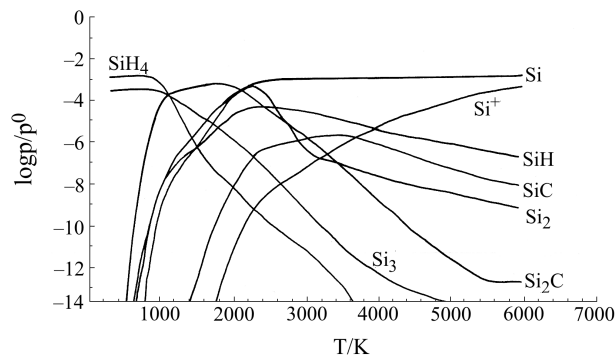


Fig. 3 Equilibrium partial pressures of silicon containing species in Ar/C/H/Si gas system, as function of temperature; C, Si = $8 \cdot 10^{-4}$, H = 0.08, $p = 1$ bar

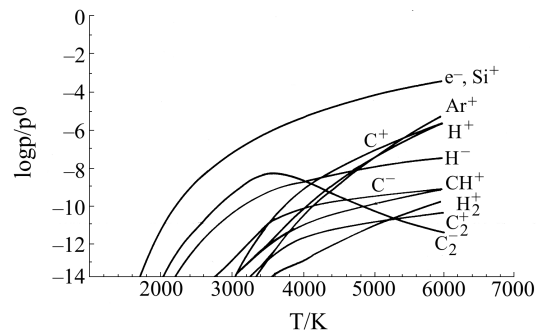


Fig. 4 Equilibrium partial pressures of ions in Ar/C/H/Si gas system, as function of temperature; C, Si = $8 \cdot 10^{-4}$, H = 0.08, $p = 1$ bar

C_2H and CH radicals. At these temperatures hydrogen is present in the system in the form of atomic hydrogen.

The equilibrium partial pressures of silicon containing compounds of Ar/C/H/Si system, as function of temperature, are shown in Fig. 3. At temperatures below 1500 K main silicon-containing compound with respect to its concentration in the plasma is SiH_4 . At temperatures between 1300–2200 K this is Si_2C . At approximately 2200 K mole frac-

tions of Si_2C and atomic Si are equal. At temperatures higher than 2400 up to 5500 K, silicon is present in the system predominantly as atomic silicon. SiC molecule appears in the plasma at 2000 K with very low partial pressure (10^{-9} bar) and reaches a broad maximum (of about 10^{-6} bar) around 3500 K. Partial pressures of ions (and electrons) as function of temperature are shown in Fig. 4. Among the ions, Si^+ appears with the highest concentration in the plasma and is the main source of electrons present in the system at temperatures discussed.

Assuming that the transition from vapour SiC (C, Si) to solid (or liquid) phase could occur when oversaturated vapour of SiC (Si, C) exists, the calculated partial pressures of SiC, Si and C, p_{SiC} , p_{Si} , p_{C} are compared with saturated vapour pressures of their counterparts, p_{SiC}^s , p_{Si}^s , p_{C}^s , and the oversaturation ratios $\gamma = p/p^s$ of SiC, Si and C as function of temperature are determined for different Ar/H/C/Si mixtures. The oversaturation ratios γ of SiC, Si and C of the particular mixture as function of temperature, are shown, as an example, in Fig. 5.

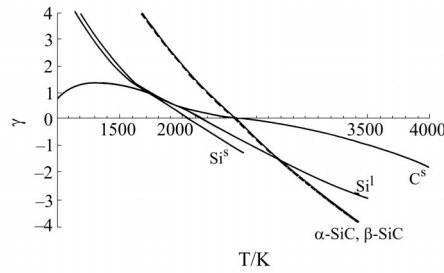


Fig. 5 The oversaturation ratios $\gamma = p/p^s$ of SiC, Si and C in Ar/C/H/Si gas system, as function of temperature; C, Si = $8 \cdot 10^{-4}$, H = 0.08, $p = 1$ bar

Equilibrium pressures of saturated vapours of SiC molecule and of Si and C atom, corresponding to heterogeneous equilibria:



as function of temperature are presented in Fig. 6. The subscripts g , s , l in Eq. (6), indicate gas, solid and liquid phase, respectively. The equilibrium partial pressures of saturated vapours (p_{SiC}^s , p_{Si}^s , p_{C}^s) are functions of temperature only and can be obtained by means of the formulae:

$$\ln p_{\text{SiC}}^s = \frac{G_{\text{SiC}(s)}^0 - G_{\text{SiC}(g)}^0}{RT}; \quad \ln p_{\text{Si}}^s = \frac{G_{\text{Si}(l)}^0 - G_{\text{Si}(g)}^0}{RT}; \quad \ln p_{\text{C}}^s = \frac{G_{\text{C}(s)}^0 - G_{\text{C}(g)}^0}{RT} \quad (7)$$

where $G_{\text{SiC}(s)}$ and $G_{\text{SiC}(g)}$, $G_{\text{Si}(l)}$ and $G_{\text{Si}(g)}$, $G_{\text{C}(s)}$ and $G_{\text{C}(g)}$ are standard Gibbs energies corresponding to solid SiC, SiC in gas phase, liquid Si, Si in gas phase, solid C, and C in gas phase, respectively.

From diagrams like those shown in Fig. 5, the saturated temperatures T^s are determined. At the saturation temperature the partial pressure of a component in the mixture is equal to its saturation vapour pressure. It also means that at the tempera-

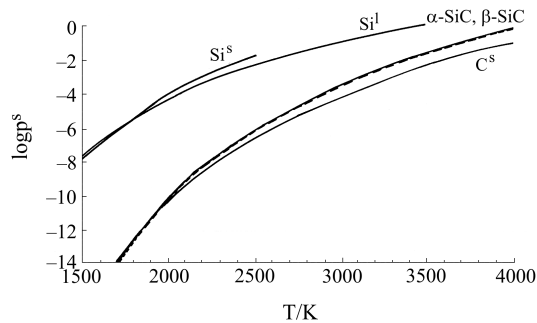


Fig. 6 Equilibrium pressures for saturated vapors of the SiC molecule (SiC^s) and the Si atom (Si^s , Si^l), C atom (C^s) corresponding to the heterogeneous equilibria, $\text{SiC}_g \leftrightarrow \text{SiC}_s$, $\text{Si}_g \leftrightarrow \text{Si}^l$, $\text{Si}_g \leftrightarrow \text{Si}^s$ and $\text{C}_g \leftrightarrow \text{C}_s$, as a function of temperature; s , l , g denote solid, liquid and gas phase, respectively

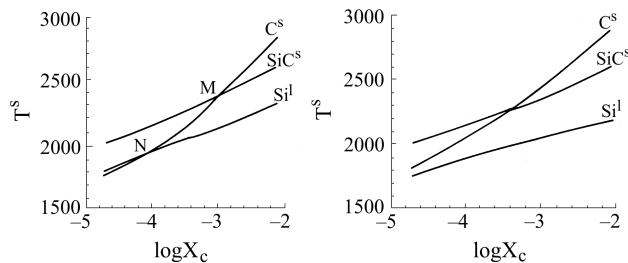


Fig. 7 Saturation temperatures of SiC, C and Si as a function of mole fraction of carbon for Ar/C/H/Si gas mixtures at C:Si = 1:1 and $p = 1$ bar (left); $p = 0.25$ bar (right)

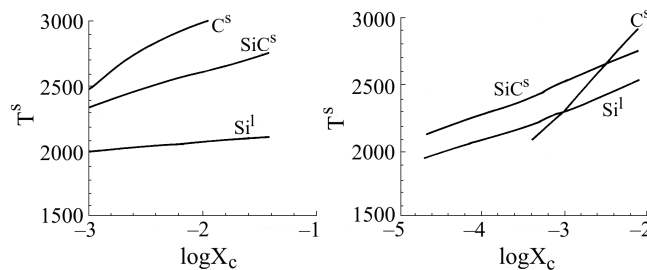


Fig. 8 Saturation temperatures of SiC, C and Si as a function of mole fraction of carbon for Ar/C/H/Si gas mixtures at C:Si = 5:1 and $p = 1$ bar (left); C:Si = 1:2, $p = 1$ bar (right)

tures lower than the saturation, $T < T^s$, the vapour of the investigated component is 'oversaturation'. The saturation temperatures determined for SiC, Si and C are presented as functions of the mole fraction of total carbon in the mixture (temperature-composition diagrams) for Si/C = 1 and total pressure of 1 bar in Fig. 7 (left), and for Si/C = 1 and total pressure 0.25 bar in Fig. 7 (right). The same type of dependence is shown for Si/C = 0.20 in Fig. 8 (left), and for Si/C = 2 in Fig. 8 (right) at the total pressure in the system of 1 bar.

Discussion

The synthesis of solid SiC becomes possible if the gas mixture with definite content of carbon and silicon at definite temperature is oversaturated with respect to the SiC vapour pressure. If the oversaturation ratio is high enough, the transformation of SiC as vapour into solid SiC can occur. As a consequence of the formation of solid SiC, the amount of SiC in the gas phase is lowered and the equilibrium ratios of Si, SiC, Si₂C and/or C in the following (or similar) gas phase reactions:



are disturbed. To reestablish these equilibriums (according to the Le Chatelier's principle) the reactions (8) are shifted to the right by additional dissociation of hydrocarbons (C₂H₂, C₂H) and silicon and carbon containing species (Si₂C, Si₂, ...), leading to deposition of solid SiC until the heterogeneous equilibrium is completed:



The partial pressures of other silicon species (Si, Si₂, Si₃ etc.) in the gas phase are now determined by partial pressures of SiC arising from heterogeneous equilibrium (9), and the partial pressure of atomic carbon (under constant total pressure of 1 bar). If the partial pressure of carbon is maintained on saturated vapour pressure level p_C^s , the amount of silicon in the gas phase can be drastically lowered (to a few percent of amount introduced) on account of formation of solid SiC. It can be concluded that practically all silicon introduced into system is converted into solid SiC. It should be mentioned that the bond distances of SiC in the gas and the solid phase are quite similar, 1.72 and 1.88 Å, respectively, what supports the proposed mechanism. The necessary conditions for the above proposed mechanism of the synthesis of SiC are:

- Sufficiently high oversaturation ratio for SiC;
- Sufficiently high temperature to ensure chemical reactions in the gas phase;
- No other component of the given gas mixture (Si, C) at definite temperature but only SiC is oversaturated.

From Figs 7 and 8 (right) it can be seen that there are mixtures (with particular amounts of Si and C and their amounts ratio) satisfying the before mentioned conditions. These are, for example, mixtures with Si:C = 1:1 having mole fraction of total carbon, x_C , in the range between x_M and x_N , corresponding to points *N* and *M* in Fig. 7 (left), at saturation temperatures of C. The mixtures with Si:C = 2:1, Fig. 8 (right), with mole fraction x_C lying between abscissa of intersecting points of curve C^s with SiC^s and Si^l curves (superscripts and l mean solid and liquid phase, respectively) also satisfy the above mentioned conditions.

Temperature saturation curve for carbon in mixtures containing carbon (silicon) in amounts larger than mole fraction at the point *M* in Fig. 7 (left) lies above the curve of SiC, indicating that there are no temperatures regions with SiC vapour as the only oversaturated one. However, since the slope of the oversaturation ratio curve of SiC (Fig. 5) is steeper than that of C, it could happen that the oversaturation ratio of SiC is

the only one sufficiently high for formation of solid phase. Generally, the formation of solid carbon is a process which competes with the deposition of solid SiC and diminishes its purity.

Under the temperature saturation curve of silicon, at temperature ~ 2000 K in the Ar/C/H/Si mixture with $6 \cdot 10^{-4}$ mole ratio of carbon and Si:C = 2:1, $p = 1$ bar [Fig. 8 (right)], the formation of Si in liquid form becomes possible. In this case the reaction:



could occur. However, thermodynamically (lower ΔG) the reaction (9) is favoured compared to (10) at this temperature. So, the formation of liquid silicon (if possible) is a process which also competes with the deposition of solid SiC.

The effect of total pressure in the system could be seen from Fig. 7 (left and right). Since the processes of dissociation are favoured by lowering of pressure, the synthesis of SiC should be performed at higher pressure.

Results of this computation are in qualitative agreement with the experimental results presented in paper [7]. It was shown in [7] that the efficiency of the synthesis and the quality of the synthesized SiC powder depended on reactant injection position, plasma power level (i.e. temperature), reactor configuration and C/Si ratio. The amount of free carbon and/or free silicon was correlated with the C/Si ratio. It was found that increase of temperature generally favours the synthesis of SiC. Lining of the cylindrical reactor wall with graphite resulted in the improved conversion to SiC. This could mean that in that way the vapour pressure of carbon is maintained on saturated vapour pressure level, p_C^s . As a useful guidance in plasma synthesis, the equilibrium composition of a particular Ar/H/C/Si mixture at established heterogeneous equilibrium (9) was calculated in [7].

Conclusions

From the calculated equilibrium compositions of Ar/H/C/Si gas mixtures follows that SiC molecules are formed between 2000–4000 K with almost constant but low partial pressure (approximately two orders of magnitude lower than total pressure of all silicon-containing species present in the system). Nevertheless, SiC vapour is in definite temperature regions of particular Ar/H/C/Si gas mixtures oversaturated, what is summarized in temperature-composition diagrams shown in Figs 7 and 8. When the SiC vapour is the only oversaturated one [as for example in the Ar/H/C/Si gas mixture with $1.5 \cdot 10^{-3}$ mole fraction of total carbon, with C:Si = 1:2 and mole fraction of hydrogen of 0.08 (the rest to 1 is argon)], at $T=2400$ K (saturation temperature of carbon) and at total pressure of 1 bar, Fig. 8 (right), the transformation of oversaturated vapour of SiC into solid SiC via above mentioned reaction route can occur. Assuming the heterogeneous reaction (9) to be completed and the partial pressure of carbon atoms to be equal to their saturated vapour pressure, almost all silicon introduced into system would be converted into solid SiC.

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