

High temperature sintering of SiC with oxide additives: I. Analysis in the SiC–Al₂O₃ and SiC–Al₂O₃–Y₂O₃ systems

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Abstract

The vaporization behaviour of pure Al₂O₃, Y₂O₃ and SiC as well as SiC–Al₂O₃ and SiC–Al₂O₃/Y₂O₃ mixtures has been analysed by thermodynamic calculations in an open system. Pure Al₂O₃ and Y₂O₃ evaporate congruently in the 1200–2300 K temperature range. Pure SiC vaporizes in a non-congruent manner leading to graphite formation as by-product. A SiC–Al₂O₃ mixture evaporates congruently according to the main vaporization reaction, $2 \text{SiC(s)} + \text{Al}_2\text{O}_3\text{(s)} + \text{Al}_2\text{O(g)} \rightleftharpoons 2 \text{SiO(g)} + 2 \text{CO(g)} + 4 \text{Al(g)}$, but the overall composition changes: for SiC rich samples, the mixture tends towards pure SiC in time, and for Al₂O₃ rich samples towards pure Al₂O₃. A SiC–Al₂O₃/Y₂O₃ mixture shows similar behaviour. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The interaction between the crucible, the powder bed and the sample in sintering of ceramic SiC compacts leads to mass variation and deposits. The nature of the underlying reactions are only poorly known. A thermodynamic analysis of the possible reactions in these systems and the vaporization behaviour should therefore help to identify the mechanisms.

The literature information is scarce and incomplete. The most thorough study has been undertaken by Misra.¹ The author calculated Pourbaix type diagrams (equilibrium phases as a function of two partial pressures) within the Si–Al–C–O system under theoretically fixed external conditions. The SOLGASMIX program has been used for the calculation and the underlying thermodynamic data has been taken from the JANAF² and the Barin/Knacke³ tables. It is important to mention that only stoichiometric compounds can be treated by this software package. Eventually, solution phases can be “approximated” by fixing activities less than unity. The author identifies four major gas species

occurring at higher temperatures in the quaternary system: SiO(g), CO(g), Al₂O(g) and Al(g). When taking Al₂O(g) and SiO(g) as axis variables and with a fixed overall carbon activity of unity (graphite is always present), a monovariant SiC–Al₂O₃ phase limit can be calculated. This phase limit has two invariant end points: Al₂O₃–SiC–SiO₂–C + gas and Al₄C₃–SiC–Al₂O₃–C + gas. The second invariant point transforms into Al₄C₃–SiC–Al₂O₃–Al(liquid) + gas if the carbon activity lowers to 0.2. A calculation of the vapour pressures along the SiC–Al₂O₃ phase boundary for both activities leads to the result, that the total pressure is minimal for the Al₄C₃–SiC–Al₂O₃–Al(liquid) + gas invariant. However this has only been demonstrated for the two activities and might be not generally true. Rocabois et al.⁴ have shown that in the case of SiC–SiO₂, this minimum lies on the binary phase limit which is probably also the case for SiC–Al₂O₃. Misra discusses in the second part of his analysis the origin of the weight loss and the gas production during the sintering process. Two situations have been distinguished by the authors:

- Sintering of SiC without free carbon present. A liquid Al or Si phase can form between 2373 and 2423 K and for a temperature higher than 2140

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K the liquid is the product of the Mullite $\text{Al}_6\text{Si}_2\text{O}_{13}$ decomposition. This stoichiometric ternary compound is formed during the reaction of SiC with Al_2O_3 .

- Sintering of SiC with the presence of excess carbon. This could lead to the occurrence of liquid phase due to the Al_2O_3 – Al_4C_3 or SiC– Al_4C_3 eutectics between 2220 and 2273 K. A Al_2O_3 – Al_4C_3 –SiC liquid phase is also a possibility.

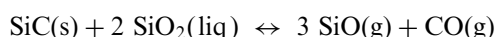
The major drawbacks of this analysis is the fixed total pressure of 1 atm and the choice of the independent gas species. A pressure of 1 bar means that the system is completely closed and a mass loss can only occur if the pressure exceeds this value. This is never true in a real sintering process. In addition to that, the solubility of SiC in the liquid phase has not been taken into account. However, this point is discussed by the author qualitatively without further justification of the conclusion because of lacking thermodynamic data. The chosen gas species $\text{Al}_2\text{O}(\text{g})$ and $\text{SiO}(\text{g})$ can never be fixed during a real sintering process, because these sensible gases are not available commercially.

A thermodynamic assessment of the Gibbs energy functions for all the phases in Y–Al–Si–C–O system has been performed by Gröbner.⁵ The goal of this study was to establish a homogeneous set of Gibbs energy data to calculate the phase diagrams in this quinary system with an emphasis on the condensed phases. The author also tried to analyse the behaviour of a SiC + $\text{Al}_2\text{O}_3/\text{Y}_2\text{O}_3$ mixture. At higher temperature, a liquid oxide will form (eutectic between YAG and Al_2O_3) which will support the sintering of the SiC sample. The gas phase evaporating from the sample is mainly composed out of $\text{SiO}(\text{g})$ and $\text{CO}(\text{g})$. This contradicts Misra's study, where Al(g) and $\text{Al}_2\text{O}(\text{g})$ were also considered as being important.

There are a few other thermodynamic analyses of the sintering process in the literature. However, these studies are less complete and the authors limit themselves very often to a few reactions and do not calculate a complete complex thermodynamic equilibrium by taking into account all the possible phases in the system.

Cordrey et al.⁶ discussed the combination SiC + Y_2O_3 sample inside a SiC + Al_2O_3 powder bed. An analysis of their samples after sintering revealed the presence of aluminium inside the sample. The partial pressures of $\text{O}_2(\text{g})$, $\text{CO}(\text{g})$, $\text{AlO}(\text{g})$ and $\text{Al}_2\text{O}(\text{g})$ are calculated at 2200 K with the assumptions of unit activities ($a_{\text{C}} = a_{\text{Al}} = 1$) and the authors concluded, that the transport from the bed to the sample is due to $\text{Al}_2\text{O}(\text{g})$ and Al(g).

Grande et al.⁷ measured the weight loss of a SiC– $\text{Al}_2\text{O}_3/\text{Y}_2\text{O}_3$ sample by thermogravimetry. In order to explain the experimental observations, two reactions are proposed:



at an initial stage because SiO_2 is always present as a contaminant at the SiC surface and:



But, this reaction alone cannot explain the observed overall weight loss. No loss of yttrium has been observed in the samples.

Gadalla et al.⁸ studied the reaction behaviour of a SiC– Al_2O_3 and a SiC–mullite mixture. By comparing the enthalpies of reaction, the authors concluded, that the gas phase over these mixtures is composed out of $\text{SiO}(\text{g})$, $\text{Al}_2\text{O}(\text{g})$ and $\text{CO}(\text{g})$.

The purpose of the present study is a complete thermodynamic analysis of the vaporization behaviour of SiC– Al_2O_3 and SiC– $\text{Al}_2\text{O}_3/\text{Y}_2\text{O}_3$ samples in an open system. The open system is defined as usually in thermodynamics: matter exchange can occur with surroundings. In this case this exchange is mainly due to leaks by the gas phase due to holes in the lid of the containers. Depending on the applied conditions, we choose two kind of leaks: (i) one kind is exchange of matter through an inert gas imposed pressure, treated as a distillation process, (ii) the second is effusion under vacuum as we shall use in mass spectrometric experiments with Knudsen cells. This work is the result of the PhD thesis of S. Baud⁹ from year 1997 to 2000.

2. Fundamentals

The evaporation behaviour of a binary compound A_mB_n in an open system, as for example a Knudsen cell under vacuum, can be classified into two groups: congruent or non-congruent. Congruent evaporation means that the atomic fluxes due to the vaporization of the compound are linked and can be described by:

$$\frac{F^{\text{at}}(A)}{F^{\text{at}}(B)} = \frac{x_A}{x_B} = \frac{m}{n} \quad (1)$$

$F^{\text{at}}(i)$ being the atomic flux of element i escaping the system and x_i the corresponding mole fraction in the resultant condensed phase.

The atomic flux of A and B are linked to the partial pressures of the different gas species according to the Hertz–Knudsen relation¹⁰ for total pressures less than 10^{-4} atm:

$$\frac{dN_i}{dt} = \frac{p_i s C}{\sqrt{2\pi R M_i T}} = F(i) \quad (2)$$

N_i being the amount of effused molecules in moles, p_i the partial pressure and M_i the molar weight of specie i . s and C are the section and the transmission coefficient (or Clausing coefficient) of the effusion orifice and R is the gas constant.

A calculation can be performed in order to determine the partial pressures which satisfy relation (1):

$$\frac{n_A(\text{gas})}{n_B(\text{gas})} = \frac{x_A}{x_B} = \frac{m}{n} \quad (3)$$

with n_i (gas) being the number of atoms of element i in the gas phase and x_i the mole fraction of i in the condensed phase. This relation is equivalent to an azeotrop in a closed system or in an atmospheric distillation process.

The first step is now to identify all the gas species formed from element A and B (A , B , $A_{m_k}B_{n_k}$) and implies the knowledge of their Gibbs energies of formation. The total flux of atom A can then be written:

$$F^{\text{at}}(A) = \sum_k m_k F_k(A_{m_k}B_{n_k}) \quad (4)$$

and with respect to the partial pressures:

$$F^{\text{at}}(A) = \frac{sC}{\sqrt{2\pi RT}} \sum_k m_k \frac{P_{A_{m_k}B_{n_k}}}{\sqrt{M_{A_{m_k}B_{n_k}}}} \quad (5)$$

This can equivalently be done for atom B.

Putting then these expressions into Eq. (1) leads to

$$\frac{\sum_k m_k \frac{P_{A_{m_k}B_{n_k}}}{\sqrt{M_{A_{m_k}B_{n_k}}}}}{\sum_j n_j \frac{P_{A_{m_j}B_{n_j}}}{\sqrt{M_{A_{m_j}B_{n_j}}}}} = \frac{m}{n} \quad (6)$$

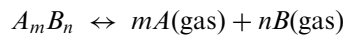
for congruent vaporization under vacuum.

For an azeotropic behaviour in a closed system, this reduces to:

$$\frac{\sum_k m_k P_{A_{m_k}B_{n_k}}}{\sum_j n_j P_{A_{m_j}B_{n_j}}} = \frac{m}{n} \quad (7)$$

This last relation can easily be verified by a thermodynamic equilibrium calculation of the vaporization of A_mB_n with a complex gas phase.

Eq. (6) can only be solved if the number of unknown variables is one, that means, one has to relate all partial pressures as a function of the partial pressure of one gas species which can be chosen arbitrarily, as for example



$$K(T) = \frac{P_A^m P_B^n}{a_{A_mB_n}} \quad (8)$$

which gives, with an activity $a_{A_mB_n} = 1$ (pure compound):

$$P_A = \sqrt[m]{\frac{K(T)}{P_B^n}} \quad (9)$$

The equilibrium constant K at a temperature T of this reaction is given as:

$$K(T) = e^{-\frac{\Delta_r G(T)}{RT}} \quad (10)$$

with $\Delta_r G$ being the Gibbs energy of reaction.

This procedure has to be continued for all gas species in the system. This links all reactions to one partial pressure (in this case P_A). Eq. (6) can then be solved within the given experimental limits, that means, 10^{-4} bar (limit of the Hertz–Knudsen equation, as mentioned above) and $P_A = P_L$, with P_L being the limiting partial pressure for the existence of the condensed compound A_mB_n that is for example A_mB_n in equilibrium with pure A . Once a solution has been found for P_A , the partial pressures of all other species can be calculated according to the supposed reactions.

This reasoning is also true for a mixture of two binary compounds: $A_mB_n + C_gD_h$. The congruent relation becomes a partial congruent relation:¹¹

$$\frac{n_A(\text{gas})}{n_B(\text{gas})} = \frac{x_A}{x_B} = \frac{m}{n} \text{ and } \frac{n_C(\text{gas})}{n_D(\text{gas})} = \frac{x_C}{x_D} = \frac{g}{h} \quad (11)$$

Both relations have to be satisfied at the same time. However, this relation is no longer equivalent to an azeotrop in a closed system, because the actual amount of effused matter can be greater for one of the two compounds, which means that the system evolves in composition along the quasi-binary A_mB_n – C_gD_h section, the gas or flow composition being in this section.

In the case of a non-congruent evaporation no solution can be found which satisfies Eqs. (6) or (11). A secondary phase is always present in such a vaporization process and one could analyse the evolution of $\frac{F^{\text{at}}(A)}{F^{\text{at}}(B)} - \frac{m}{n}$ in the different and adjacent two- or three-phase fields. In the case of a non-congruent evaporation, the sign of the resulting number is the same within the different and adjacent two- or three-phase fields.

3. Results

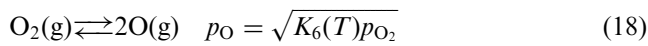
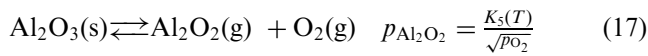
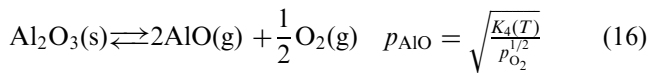
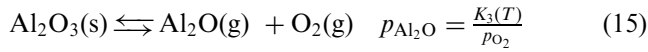
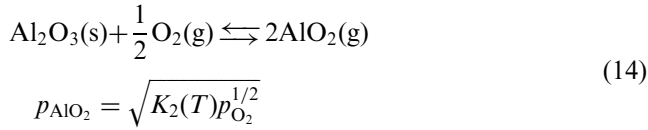
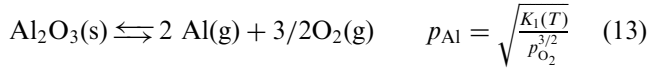
The Gibbs energy data for all the gas species have been taken from the SGTE (Scientific Group Thermo-data Europe) pure substance database.¹² The values for the condensed compounds are either from the SGTE pure substance database or from Gröbner.⁵

3.1. Al–O

Drowart et al.,¹³ Burns¹⁴ and Farber et al.¹⁵ studied the vaporization behaviour of solid Al_2O_3 in a tungsten effusion cell. They all observed a congruent evaporation of this compound:

$$\frac{F_{\text{O}}(\text{gas})}{F_{\text{Al}}(\text{gas})} = \frac{x_{\text{O}}}{x_{\text{Al}}} = \frac{3}{2} \quad (12)$$

The main gas species in the system are Al(g), AlO₂(g), Al₂O(g), AlO(g), Al₂O₂(g), O(g) and O₂(g) [O₃(g) has been neglected]. O₂(g) has been chosen as independent variable with the following reactions:



The lower limit for the oxygen partial pressure is given by the decomposition of Al₂O₃(s) into Al(s or l) and oxygen gas. The calculation has been performed in the temperature interval ranging from 1200 to 2300 K. This interval has been chosen because it includes the experimentally used temperatures in sintering process. An oxygen partial pressure satisfying the congruent relation has been determined with a temperature step of 100 K. The result for $T = 2200$ K is plotted in Fig. 1. The flux ratio $\frac{F(\text{O})}{F(\text{Al})}$ equals $\frac{3}{2}$ for an oxygen partial pressure of $5.34 \cdot 10^{-9}$ atm, which is within the interval 10^{-4} atm and $p_{\text{L}} = 4.71 \cdot 10^{-16}$ atm. It is important to notice, that the

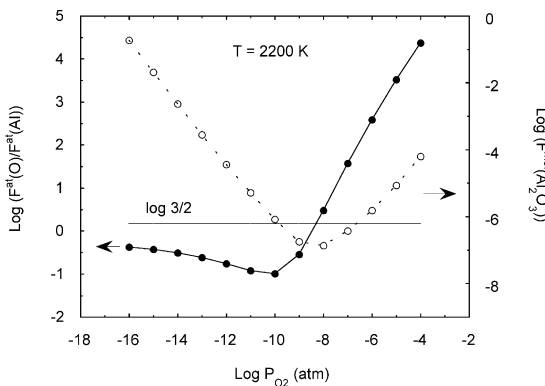
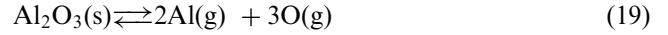


Fig. 1. Evolution of the decimal logarithm of the O to Al atomic flow ratio $\log_{10}\left(\frac{F^{\text{at}}(\text{O})}{F^{\text{at}}(\text{Al})}\right)$ and of the alumina flow $\log_{10}F^{\text{mol}}(\text{Al}_2\text{O}_3)$ as a function of the decimal logarithm $\log_{10}(P_{\text{O}_2})$ at $T = 2200$ K. The $\log 3/2$ corresponds to the congruent vaporization of alumina and the intercept with black dots gives the partial pressure of O₂(g) for this vaporization process.

total flux $F^{\text{mol}}(\text{Al}_2\text{O}_3)$ presents a minimum at that point. This is the minimum flux equivalent of the minimum pressure for an azeotrop in a closed system, but not occurring at the same oxygen activity or partial pressure because of the flow relation.

The vaporization under vacuum of Al₂O₃ is found to be congruent in the whole interval 1200–2300 K. The partial pressures of all gas species as a function of $1/T$ are represented in Fig. 2. The main gas species are Al(g) and O(g), i.e. the predominant vaporization reaction is:



These results are in good agreement with the experimental data of Drowart et al.,¹³ Burns¹⁴ and Farber et al.¹⁵

3.2. Y–O

Ackermann et al.¹⁶ and Liu et al.¹⁷ observed experimentally the congruent evaporation of Y₂O₃(s). The composition of congruent vaporization shifts slightly to Y₂O_{2.996}(s) at higher temperatures ($T > 2509$ K).¹⁷ From the SGTE database, seven gaseous species have been taken into account in addition to the condensed Y₂O₃(s) and Y(s or l) compounds: Y(g), Y₂O(g), YO₂(g), YO(g), Y₂O₂(g), O(g) and O₂(g).

For temperatures from 1200 to 2300 K, the vaporization of Y₂O₃(s) is found to be congruent with YO(g), YO₂(g) and O(g) being the major gas species. This result is in contradiction to the experimental information from the literature^{16,17} where the major congruent vaporization reaction is:

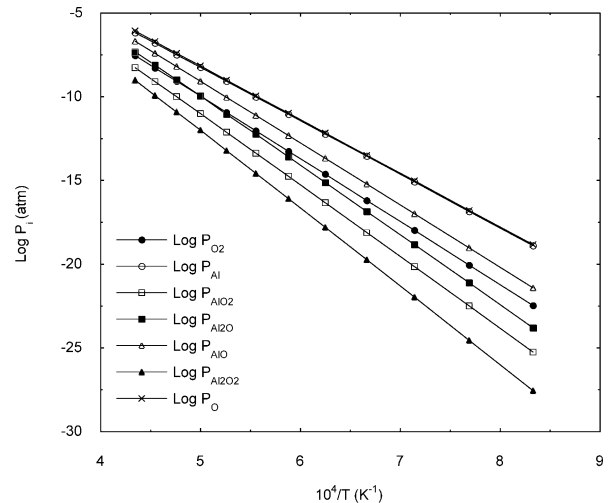
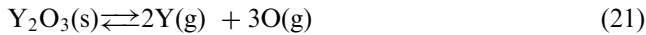


Fig. 2. Calculated decimal logarithm partial pressures for the congruent vaporization of Al₂O₃(s) in vacuum as a function of the inverse temperature $1/T$.

and a secondary reaction with minor importance (but nevertheless included in the calculations) is:



No gaseous species $YO_2(g)$ has been detected in their respective measurements indicating that the partial pressure of this species should be considerably less important ($< 10^{-6}$) than the calculated one. The same is true for $Y_2O(g)$; even in the evaporation study of a $Y(s) + Y_2O_3(s)$ mixture, in which the partial pressure of this gaseous species should be at its maximum, this molecule has not been detected.¹⁸ These two species have therefore been discarded in the calculations and the resulting partial pressures for the five others are plotted in Fig. 3, and are in agreement with the experimental observations.

3.3. Si–C

The vaporization of SiC(s) is not congruent. The gas phase is silicon rich and graphite is formed.¹⁹ In order to confirm this behaviour, calculations in the Si(s or l) + SiC(s) and C(s) + SiC(s) two phase regions have been performed. The gas species considered are Si(g), Si₂(g), Si₃(g), C(g), C₃(g), SiC(g), Si₂C(g) and SiC₂(g). Species with lower probability ($< 10^{-3}$) to occur like C₂(g), C₅(g), Si_n(g) ($4 < n < 7$) and other Si_nC_m(g) have been neglected.²⁰

The calculation of $\frac{F^{at}(Si)}{F^{at}(C)} - 1$ gives a value of 5452 at 1200 K and 3 at 2300 K for a SiC(s) + C(s) mixture and 12127 at 1200 K and 7 at 2300 K for a SiC(s) + Si(s or l) mixture. All these values are positive which confirms the non-congruent evaporation of SiC.

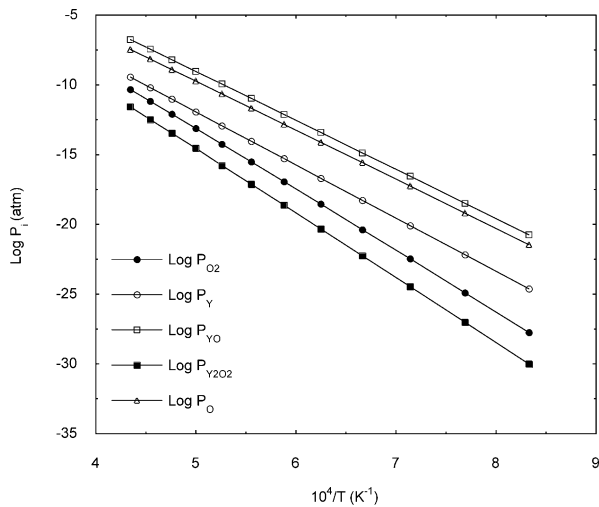


Fig. 3. Calculated decimal logarithm partial pressures for the congruent vaporization of $Y_2O_3(s)$ in vacuum as a function of the inverse temperature $1/T$.

Table 1

Stoichiometric compounds, solution phases and gas species used for the thermodynamic calculations

Solution phases ⁵	Condensed compounds ^{5,12}		Gas species ¹²		
FCC–(Al, Si)	Si	Al ₂ O ₅ Si	Al	AlC	O
(Al, Si) ₄ C ₃	Graphite	α-SiC	AlC ₂	AlO	SiO
Liquid–(Al, Si, C)	Al ₂ O ₃	β-SiC	AlO ₂	Al ₂	O ₂
	Al ₂ CO	SiO ₂	Al ₂ C ₂	Al ₂ O	SiO ₂
	Al ₂ O ₇ Si ₂	Al ₄ C ₄ Si	Al ₂ O ₂	Al ₂ O ₃	Si ₂ O ₂
	Al ₄ CO ₄	Al ₈ C ₇ Si	C	CO	O ₃
			CO ₂	SiC	Si
			Si ₂ C	C ₂	Si ₂
			C ₂ O	SiC ₂	Si ₃
			C ₃	C ₃ O ₂	Ar
			C ₄	C ₅	

3.4. Vaporization of a SiC–Al₂O₃ mixture

3.4.1. Closed system calculations

No experimental information is available on the vaporization behaviour of a SiC–Al₂O₃ mixture in vacuum. Closed system complex thermodynamic equilibrium calculations have therefore been performed using all the species summed up in Table 1 and the GEMINI 2 (Gibbs Energy Minimizer) software package.²¹ The underlying principle of these calculations is the minimization of the total Helmholtz free energy of the system for a given volume, temperature and overall composition.

The main gas species at equilibrium over a SiC + Al₂O₃ mixture in the temperature range 1700–2200 K are CO(g), SiO(g), Al₂O(g) and Al(g). Their partial pressures are plotted in Fig. 4. Up to 2150 K, only SiC and Al₂O₃ are present at equilibrium. At temperatures above this value, a silicon rich metallic liquid phase is formed additionally. The vaporization is therefore “partially” azeotropic (expression defined by

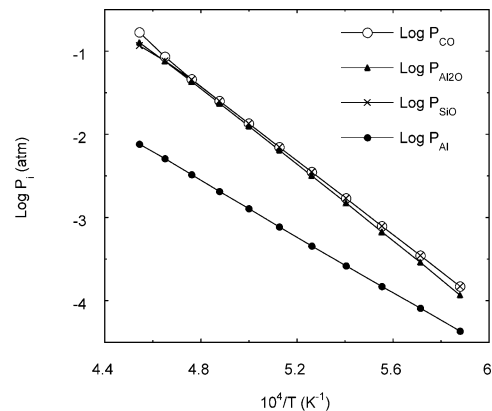
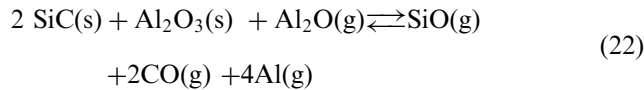


Fig. 4. Calculated decimal logarithm partial pressures of CO(g), SiO(g), Al₂O(g) and Al(g) for the azeotropic vaporization of a SiC–Al₂O₃ mixture in a closed system as a function of the inverse temperature $1/T$.

Rocabois et al.⁴⁾ below 2150 K. It is not purely azeotropic, because the gas phase over the mixture has a different composition than the solid mixture, but is in line with the SiC–Al₂O₃ section. From partial pressures, the composition of the gas phase in the pseudobinary section is calculated as 50.6% (mol) SiC, 49.4% (mol) Al₂O₃. The composition of the powder mixture is still only SiC and Al₂O₃, but their relative amounts change by vaporization along the SiC–Al₂O₃ pseudo-binary section. The overall reaction can therefore be written as:



This has consequences for an open system approach, where the composition of a powder mixture could change with time. For SiC rich mixtures (> 50.6% (mol) SiC), the system will tend to pure SiC and for Al₂O₃ rich mixture, the system will evolve towards pure alumina.

The phase diagram of the Si–Al–C–O quaternary system has been calculated for temperatures below 2150 K. A partial isothermal section of the quaternary system is presented in Fig. 5. With graphite, very often present in sintering experiments as crucible material, the main difference is a higher CO(g) partial pressure for a SiC–Al₂O₃ + C mixture. Consequently, in an open system, an evolution towards a quaternary SiC–C–Al₂O₃–Al₄O₄C mixture would be expected due to CO(g) loss, and for even higher CO(g) loss, a mixture of SiC–C–Al₂O₃–Al₄SiC₄ could be attained as shown by an arrow in Fig. 5.

3.4.2. Open system calculations

In order to verify a congruent vaporization behaviour of a SiC–Al₂O₃ mixture, open system calculations have been performed in analogy to the pure binary systems discussed previously.

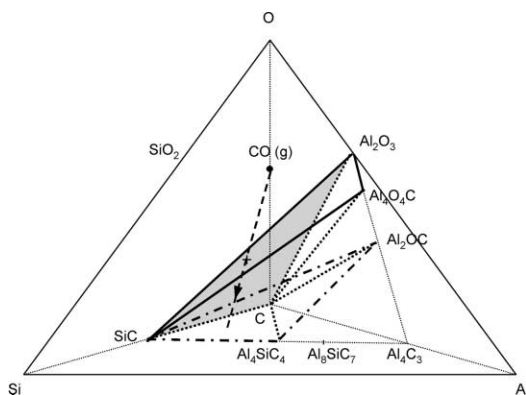


Fig. 5. Calculated partial isothermal section ($T < 2200$ K) of the Si–Al–C–O system showing the possible evolution of a SiC–Al₂O₃–C condensed phases mixture during vaporization in an open system.

The congruent condition becomes:

$$\frac{F^{\text{at}}(\text{O})}{F^{\text{at}}(\text{Al})} = \frac{3}{2} \text{ and } \frac{F^{\text{at}}(\text{Si})}{F^{\text{at}}(\text{C})} = 1 \quad (23)$$

The gas species taken into account are the same than in the closed system calculations (Table 1). The vaporization of a SiC–Al₂O₃ mixture is found also congruent in an open system for temperatures in the range 1200–2170 K. The main gas species are Al(g), SiO(g), CO(g) and Al₂O(g) and their resulting partial pressures are plotted in Fig. 6. The partial pressures of Al(g), SiO(g) and CO(g) are close together. At lower temperature $P_{\text{Al}} > P_{\text{SiO}} > P_{\text{CO}}$ (Fig. 6d), in the midrange of the temperature interval, $P_{\text{SiO}} > P_{\text{Al}} > P_{\text{CO}}$ (Fig. 6c) and for the high temperature region $P_{\text{SiO}} > P_{\text{CO}} > P_{\text{Al}}$ (Fig. 6b). It is important to mention that conversely to the closed system, the partial pressure of Al(g) under Knudsen conditions is much higher than the one of Al₂O(g), the partial pressures of these two species being inverted.

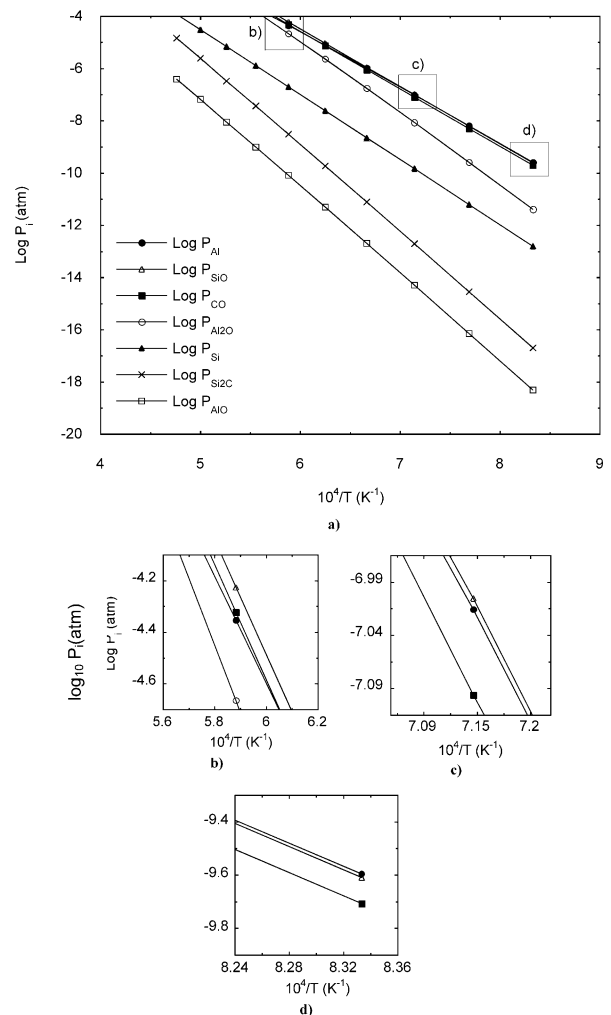


Fig. 6. Calculated decimal logarithm partial pressures for the congruent vaporization of a SiC–Al₂O₃ mixture in vacuum as a function of the inverse temperature $1/T$.

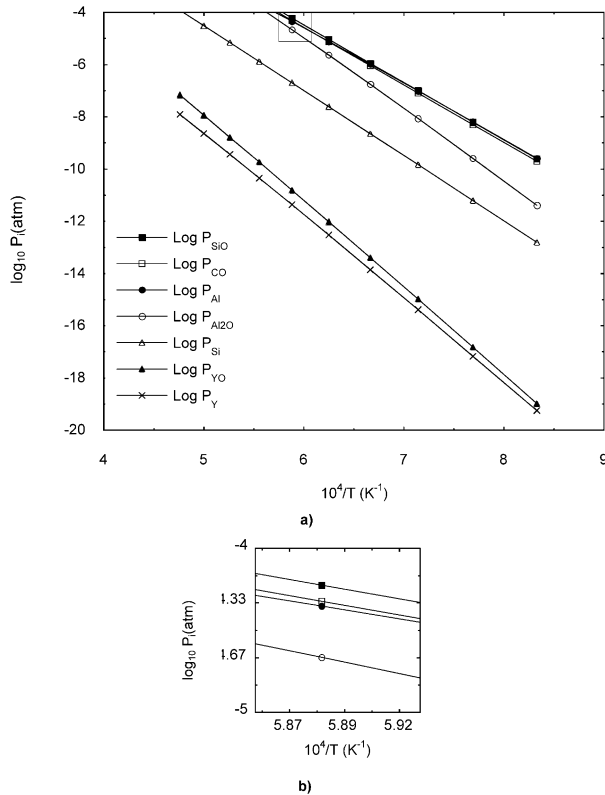


Fig. 7. Calculated decimal logarithm partial pressures for the congruent vaporization of a SiC–Al₂O₃/Y₂O₃ mixture in vacuum as a function of the inverse temperature 1/T.

The silicon activity has been calculated as a function of temperature. It increases monotonically with temperature until it reaches a maximum ($a_{\text{Si}} = 1$) at 2170 K. At this temperature, liquid silicon is formed which makes the vaporization no longer congruent within the quasi-binary SiC–Al₂O₃ section.

3.5. Vaporization of a SiC–(Al₂O₃/Y₂O₃) mixture

The conditions for a congruent vaporization of a SiC–(Al₂O₃/Y₂O₃) mixture are the following:

$$\frac{F^{\text{at}}(\text{O})}{F^{\text{at}}(\text{Al})+F^{\text{at}}(\text{Y})} = \frac{3}{2} \text{ and } \frac{F^{\text{at}}(\text{Si})}{F^{\text{at}}(\text{C})} = 1 \quad (24)$$

As for the SiC–Al₂O₃ mixture, both relations have to be respected simultaneously. The same gas species as for the previous calculations plus Y(g), YO(g) and Y₂O₂(g) have been used for the simulation.

The vaporization is again congruent between 1200 and 2100 K showing a similar behaviour to a pure SiC–Al₂O₃ mixture. The resulting partial pressures for an open system are plotted in Fig. 7. As before, Al(g), SiO(g), CO(g) and Al₂O(g) are the main species, with Y(g) and YO(g) being present in a minor way. Pure Y₂O₃(s) ($a_{\text{Y}_2\text{O}_3} = 1$) has been considered in our calculations for simplification. In a real system, Al₂O₃ and

Y₂O₃ would react to form either the YAG compound or a oxidic liquid phase. In both cases the activity of Y₂O₃ would be less than unity, resulting in even smaller Y(g) and YO(g) partial pressures. The activity of Al₂O₃ would however stay close to unity and the system vaporization behaviour would be basically the same.

The silicon activity is again increasing with temperature, leading to a non-congruent effusion behaviour for temperatures above 2170 K. The SiC–(Al₂O₃/Y₂O₃) mixture would become silicon rich.

4. Conclusion

The causes and the way of the matter losses in the sintering of SiC with oxidic additives (Al₂O₃, Y₂O₃) has been analysed by thermodynamic calculations. An open system approach using either distillation conditions or the Hertz–Knudsen equation has been used to compute the atomic fluxes and to trace the partial pressures of the main gas species as a function of 1/T in the 1200–2200 K temperature range.

Pure SiC evaporates in a non-congruent manner leading to graphite formation. Pure Al₂O₃ and Y₂O₃ show congruent vaporization. A SiC–Al₂O₃ mixture also vaporizes congruently, i.e. the composition of the solid phase and the gas phase lies on the SiC–Al₂O₃ quasi-binary section. However, the relative amounts of the constituent solid compounds change with time. For SiC rich samples, the mixture tends towards pure SiC in time, and for Al₂O₃ rich samples towards pure Al₂O₃. The main gas species are Al(g), Al₂O(g), SiO(g) and CO(g) in equivalent partial pressures and an overall vaporization reaction: $2 \text{SiC}(\text{s}) + \text{Al}_2\text{O}_3(\text{s}) + \text{Al}_2\text{O}(\text{g}) \leftrightarrow \text{SiO}(\text{g}) + 2 \text{CO}(\text{g}) + 4 \text{Al}(\text{g})$ can be proposed. When taking into account additional graphite (e.g. the crucible), the CO(g) partial pressure increases and additional phases like Al₄O₄C, Al₂OC or Al₄SiC₄ can occur. The vaporization of a SiC–Al₂O₃/Y₂O₃ mixture shows a similar behaviour. These results will be confirmed by mass spectrometric measurements of the gas phase composition which will be subject of part II to IV.^{22–24}

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