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System Si–Al–Mg–O: Thermodynamic Aspects of its Influence on the Oxidation Resistance of Silicon Carbide at High Temperature

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Abstract

With the aim to protect silicon carbide based materials against oxidation at high temperature, the influence of silica-based refractory glasses is examined through thermodynamic equilibrium calculations. The systems Si–Al–Mg–O and Si–Al–Mg–O–C are considered. The thermodynamic data for the ternary liquid phase are obtained through a 'cells' model. The vaporization behaviour of different slag compositions (2000–2250 K) are deduced from heterogeneous calculations and from comparison with pure silica. Trends of lowering the vaporization and the reactivity against silicon carbide are strongly related with the amount of alumina and magnesia in the liquid phase.

Unter dem Gesichtpunkt Materialen, die auf Siliziumcarbid basieren, gegen Oxidation bei hohen Temperaturen zu schützen, wird die Bedeutung von hitzebeständigen Silikatgläsern mit Hilfe von thermodynamischen Gleichgewichtsberechnungen bestimmt. Es werden die Systeme Si–Al–Mg–O und Si–Al–Mg–O–C betrachtet. Die Daten der pseudoternären Flüßigphase werden mit Hilfe eines 'Zellen'-Modells berechnet. Das Verhalten bei hohen Temperaturen (2000K–2250K) und die Verdampfung der Schlacken verschiedener Zusammensetzung werden aus der Zusammensetzung der Gasphase im Gleichgewicht abgeleitet, und mit dem Verhalten von reinem Silikat verglichen. Es zeigte sich, daß die Zugabe von Aluminiumoxid und Magnesiumoxid zur flüssigen Phase die Verdampfung der Schlacke stark vermindert und ihre Reaktivität bezüglich Siliziumcarbid herabsetz.

Dans l'optique de protéger les matériaux à base de carbure de silicium contre l'oxydation à haute température, l'intérêt des verres réfractaires à base de silice est examiné par le biais de calculs à l'équilibre thermodynamique. Les systèmes Si–Al–Mg–O et Si–Al–Mg–O–C sont étudiés et les données thermodynamiques concernant la phase liquide pseudoternaire font appel à un modèle en 'cellules'. Le comportement à haute température (2000–2250 K) et la volatilisation de laitiers de différentes compositions sont déduits de la composition de la phase gazeuse à l'équilibre et comparés au comportement de la silice pure. Il est établi que l'addition d'alumine et de magnésie dans la phase liquide diminue fortement la volatilisation du laitier ainsi que sa réactivité vis à vis du carbure de silicium.

1 Introduction

In order to use carbon–carbon, SiC–SiC or SiC–C composites in high-temperature structural applications above 1800°C, the challenge is to improve considerably the oxidation resistance. Although extensive studies have been carried out in the past decade, the problem has not yet been solved successfully with regard to the constraints connected with aerospace applications.

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With such a purpose in mind, it seems unrealistic to foresee a protection system which would not be constituted by an outside oxide layer, the latter being either a suitable coating or the result of the conversion of the well-known oxidation-resistant silicon carbide. This latter case is the classical method but suffers from lack of performance above 1400°C. In a recent overview,[1] the authors discuss some problems in relation with two types of protection—solid oxides and viscous oxides. The oxidation of SiC to give a protective layer of molten silica falls into the second class and undoubtedly offers several positive features such as layer strain accommodation, potential sealing of cracks due to the viscous properties of the product and low oxygen diffusivity. Therefore, the way to enhance the long-term oxidation resistance through silica-based refractory glasses can be examined. At very high temperature it is well known that:(i) the reactivity (vaporization processes/formation of volatile products) either with the gaseous environment or the material to be protected becomes dominant, (ii) thermodynamic limitations may become important, and (iii) the experimental data are scarce, costly and difficult to obtain. For these reasons, an aid in predicting the chemistry may have a large impact on the experiments to be carried out. The purpose of this work is to illustrate the chemical behaviour of glasses or liquid phases by thermodynamic equilibrium calculations in a high-temperature range

2 Choice of the System

There are few binary oxides which must be considered (on the basis of thermal stability and vapour pressure) for an oxidation protection at very high temperature: BeO, Sc_2O_3, Y_2O_3, ZrO_2, HfO_2, Al_2O_3, SiO_2. Among them, SiO_2 exhibits the lowest melting point, and such a compound can be generated by different methods from thin to thick coatings without any difficulties even on large sized shapes. On the other hand, it combines with a great variety of other binary oxides leading to polycationic systems which have been largely studied from the structural and phase diagram points of view, due to their developments in ceramic applications and in the metallurgy field where they are encountered as slags. Based on all these arguments, it is worth considering SiO_2 as a basis and examining how to modify its behaviour by addition of other oxides in order to get a homogeneous liquid phase with higher viscosity and lower volatility and to provide the lowest possible oxygen auto-diffusion coefficient. Al_2O_3 seems to be able to fulfil these requirements. Furthermore the phase diagram is well known and exhibits the presence of mullite phase (3 Al_2O_3–2 SiO_2) which has a low thermal expansion coefficient ($5{\cdot}3 \times 10^{-6}$ K^{-1}).[2] It is noteworthy that mixtures of mullite + silica must exhibit a favourable rheological behaviour under intense gaseous fluxes. As a matter of fact they are industrially used in ceramic furnaces as firing indicators. Nevertheless, data on volatility were not encountered, thus reinforcing the interest in predicting the vaporization ability and in analysing the role of Al_2O_3 addition to SiO_2. In order to establish whether the improvement associated with an oxide addition can be a cumulative effect, a third constituent was considered. The most attractive one seems to be MgO. The pseudo-ternary phase diagram SiO_2–Al_2O_3–MgO presented in Fig. 1[3] is one of the best known ternary systems based on silica. Besides a large extent of the liquidus line in the temperature range of interest (1700–2000°C) it includes the cordierite phase (5 SiO_2–2 Al_2O_3–2 MgO), which is well known for its thermal shock resistance and low thermal expansion coefficient ($1{\cdot}7 \times 10^{-6}$ K^{-1}): cordierite glasses with zero expansion have also been reported earlier.

In summary, thermodynamic calculations were carried out in the systems Si–Al–Mg–O and Si–Al–Mg–O-C.

3 Calculation Method and Input Data

To the authors' knowledge equilibrium calculations related to determination of the vapour-phase compositions above these ternary liquids have not so far been reported. Concerning the present system, only studies related to condensed compounds and subsolidus phase equilibria were carried out.[4–6]

3.1 Description of the system

Since the aim is to perform calculations at very high temperatures (1800–2300 K), the system must comprise the gaseous phase including all the components that are able to form from the considered atomic system, the condensed phases either solid or liquid ones. Hence, the following species were considered in the gaseous phase: Si(g), Si_2(g), Si_3(g), SiO(g), SiO_2(g), SiC(g), Si_2C(g), SiC_2(g), Al(g), AlO(g), Al_2O(g), AlO_2(g), Al_2O_2(g), AlC(g), Mg(g), CO(g), CO_2(g), O_2(g). The condensed species were the solids C(graphite), SiO_2(s), Al_2O_3(s), MgO(s), 2 SiO_2–3 Al_2O_3(mullite), SiO_2–MgO(protoenstatite), SiO_2–2MgO(forsterite), Al_2O_3–MgO(spinel), SiC(s), Al_4C_3(s), the liquids Si(l), Al(l), Mg(l) and the liquid mixture of oxides (or

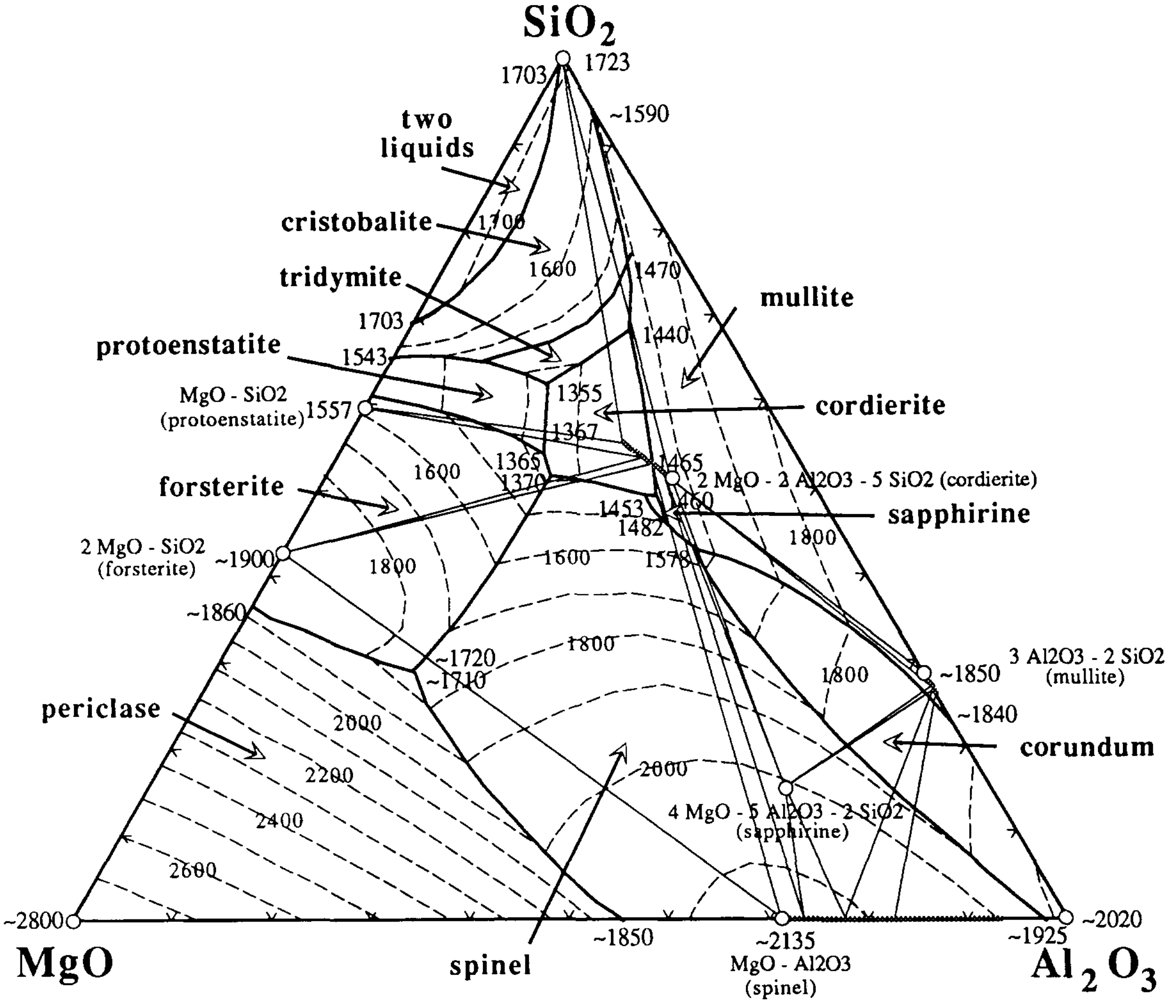

Fig. 1. Pseudo-ternary phase diagram SiO_2–Al_2O_3–MgO (wt% coordinates).

slag) which needs a specific description presented later. The non-stoichiometry of mullite, spinel and periclase solid solutions were not taken into account, due to their narrow homogeneity range and existence field in the phase diagram (see Fig 1). On the other hand, due to the lack of basic data, it is impossible to model the phase diagram domain where liquid–liquid separation occurs.

3.2 General method of calculation

The computation program MELANGE,[7] commercially available now as GEMINI2 from Thermodata (BP66, 38402 Saint Martin d'Hères, France) was used for the calculation of the chemical equilibrium from different input parameters (temperature T, total pressure P, composition). This classical method minimizes the total Gibbs energy of the system, taking into account the mass balance constraints. The specific feature of the program is to enable the introduction (by subroutine systems) of any model in order to describe the thermodynamic properties of mixtures. Any user can choose (as required) the form of the excess Gibbs energy for each phase in solution. The input thermodynamic data are standard Gibbs energy of formation for all the considered compounds.

3.3 Description of the complex liquid phase and data

For the gaseous chemical and the condensed species, thermodynamic data come from the assessed bank Thermodata. For the complex liquid, an estimation was made. Therefore, with this set of data, it was checked that for several given atomic compositions, the equilibrium compositions calculated by minimization of the total free energy at different temperatures indicate the disappearance of the liquid phase at temperatures in agreement with the experimental liquidus curve.

The formalism used for the liquid phase is based on a thermostatistical model which was previously applied to metallurgical slags[8] in the laboratory of one of the authors. This formalism is suitable to describe strong interactions and furthermore treats the Redlisch–Kister polynomial representation. This model assumes that the thermodynamics for solutions are ruled by binary interactions (a valid assumption whatever the solution is: ionic, metallic or covalent). All equilibrium calculations need the knowledge of the conventional Gibbs free energy function for each species.

For any solid solution or liquid phase, this is expressed by:

$$G = G^0 + G^{id} + G^{xs} \quad (1)$$

where G^0 corresponds to the formation of specific entities in the phase from the elements in their standard state, G^{id} is related to the formation of an ideal solution from the specified entities (no interaction among them), and G^{xs} is the excess term describing the interactions.

The classical steps are to define an identical reference state for all the phases, then to express their free energy change G^0, and to estimate G^{id} and G^{xs} through a solution model based on peculiar entities (ions, atoms, molecules, 'cells', etc.) needed for an adequate description of the involved phase.

In the present case, at any temperature, the components of the system were considered in their reference state: Si(l), Al(l), Mg(g), O_2(g) and C(graphite).

The melt SiO_2–Al_2O_3–MgO is a mixture of 'cells', regarded as quasi-components, which are $Si_{1/2}O$, $Al_{2/3}O$, MgO, $Si_{1/4}Mg_{1/2}O$, $Al_{1/2}Mg_{1/4}O$ according to Saint-Jours.[8] The free energy of each 'cell' is calculated from the Gibbs free energy of oxides SiO_2(l), Al_2O_3(l) and MgO(l) classically expressed by:

$$G^0(\text{oxide},l) - G^0(\text{oxide},s) = L_f\,(1 - T/T_f) \quad (2)$$

where T and T_f are the absolute temperature and the oxide melting point respectively, L_f is the latent heat of fusion. The Gibbs free energy of the liquid phase is then expressed as a function of the i 'cell' concentration ($y_i = n_i/n$) in the solution:

$$G^0 = \sum_i y_i\, G^0(i) \quad (3)$$

It comes out an ideal solution free energy change given by:

$$G^{id} = \sum_i y_i\, RT \log(y_i) \quad (4)$$

The free energy excess term is expressed by a Redlisch–Kister polynomial model:

$$G^{xs} = \sum_{ij} y_i y_j [\varepsilon^0_{ij} + \varepsilon^1_{ij}(y_i - y_j)] \quad (5)$$

where ε^0_{ij} and ε^1_{ij} are interaction parameters between the 'cells' i and j. These excess parameters were obtained from calculations in order to fit the liquidus temperature with the experimental values. Table 1 lists the excess coefficients determined in the case of the ternary liquid mixture SiO_2–Al_2O_3–MgO with the five different 'cells', four interaction coefficients being considered to describe satisfactorily this liquid phase.

This is illustrated in Fig. 2 which compares the calculated liquidus at 2000K (dashed line) to the experimental one.[3] The SiO_2-rich corner (two liquids domain) is not to be considered. No attempt has been made to approach the real state better with another description and these data were used, in connexion with the data for gases and solids (see Table 2), for calculations in the Si–Al–Mg–O–C system.

Table 1. Excess coefficients corresponding to eqn (5).

Cell i	*Cell j*	*Epsilon 0 (J)*	*Epsilon 1 (J)*
Si 0·5 O	Al 0·67 O	32 360	
Si 0·5 O	Mg O		
Si 0·5 O	Si 0·25 Mg 0·5 O	10 470	41 860
Si 0·5 O	Al 0·5 Mg 0·25 O		
Al 0·67 O	Mg O		
Al 0·67 O	Si 0·25 Mg 0·5 O		
Al 0·67 O	Al 0·5 Mg 0·25 O	29 300	
Mg O	Si 0·25 Mg 0·5 O		
Mg O	Al 0·5 Mg 0·25 O	25 120	
Si 0·25 Mg 0·5 O	Al 0·5 Mg 0·25 O		

Table 2. Thermodynamic data considered for the calculations

		delta G = A + B T (J/mol)	
	Compound	*A (J/mol)*	*B (J/mol/K)*
Gases	Si	391286·1	−112·226
	Si_2	471505·6	−114·4574
	Si_3	455093·8	−93·50057
	SiO	−164844·8	−45·11
	SiO_2	−362081·6	31·79929
	SiC	663133·9	−157·36
	Si_2C	432255·5	−126·553
	SiC_2	560387·1	−169·6124
	Al	299984·8	−108·9225
	AlO	57613·07	−57·98917
	Al_2O	−184376·9	−40·78204
	AlO_2	−204138·4	8·937746
	Al_2O_2	−453850·3	52·1379
	AlC	657898·4	−158·1443
	Mg	0	0
	MgO	−1459·892	33·34544
	CO	−119150	−83·39405
	CO_2	−396031·5	0·01563846
	O_2	0	0
Liquids	Si	0	0
	Al	0	0
	Mg	−116·9205	85·6905
	Si 0·5 O	−467338	95·87762
	Al 0·67 O	−519116·7	89·5526
	Mg O	−653974	179·8362
	Si 0·25 Mg 0·5 O	−576943·3	136·7227
	Al 0·5 Mg 0·25 O	−382009·2	112·1235
Solids	SiO_2	−944220	196·527
	Al_2O_3	−1674296	319·2903
	MgO	−728396·2	203·7915
	$2(SiO_2)3(Al_2O_3)$	−68·86079	132·6853
	$(SiO_2)\,(MgO)$	−1703779	402·3764
	$(SiO_2)\,2(MgO)$	−2378740	565·9814
	$(Al_2O_3)\,(MgO)$	−2424341	515·3765
	SiC	−120969·4	37·2569
	Al_4C_3	−265480	95·32373
	C	0	0

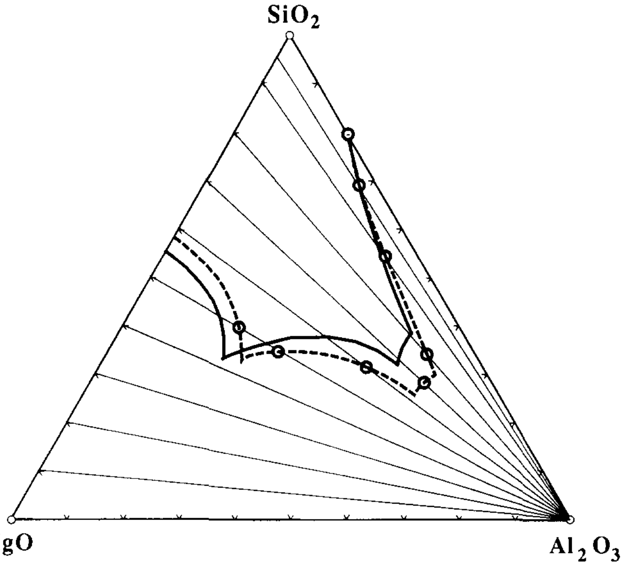

Fig. 2. Comparison of experimental (——) and calculated (- - -) liquidus lines at 2000 K in the pseudo-ternary system SiO_2–Al_2O_3–MgO (wt% coordinates).

4 Applications and Discussion

4.1 Vaporization in the system Si–Al–Mg–O

In order to prove the influence of a complex liquid oxide with regard to pure SiO_2, thermodynamic calculations from 100 moles of a starting mixture (x SiO_2–y Al_2O_3–z MgO) and 1 mole of gaseous environment (0·2 O_2–0·8 Ar) at constant temperature (2250 K) and constant total pressure (10^{-3} atm) were carried out. The equilibrium composition in the gas phase was then compared with the one over pure SiO_2 by means of a ratio $R = C/D$, where $C = n_1$ SiO(g) + n_2 SiO_2(g) + n_3 MgO(g) + n_4 Mg(g), that is, the sum of the mole numbers of the four main gaseous species above the condensed phases, and where $D = n'_1$ SiO(g) + n'_2 SiO_2(g) has an identical meaning above pure silica for the same input conditions. Such a ratio is a signature of the vaporization behaviour.

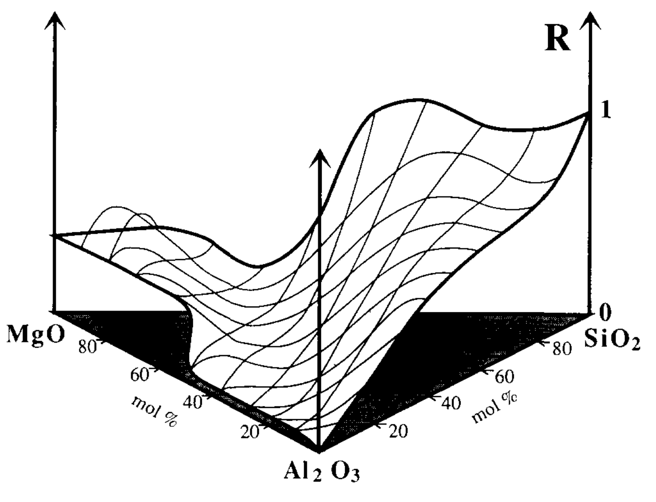

Fig. 3. Evolution of the R gas phase ratio (vaporization) as a function of the condensed phases composition at 2250 K.

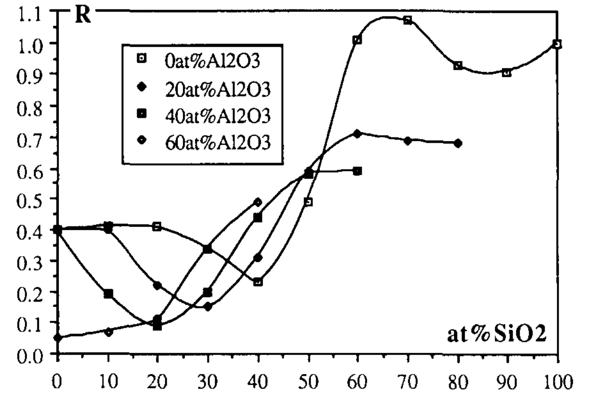

Fig. 4. Variation of the gas phase ratio R (vaporization) versus the SiO_2 content of the condensed phases at 2250 K.

Calculations were made for constant fractions of Al_2O_3 and MgO in the starting mixture respectively. Figure 3 shows the R variations in relation to the pseudo-ternary compositions. Figure 4 summarizes variations versus the SiO_2 content for some selected fixed Al_2O_3 contents. With regard to pure SiO_2, the decreasing trend in vaporization is obtained for the different screened compositions. As an example, in the pseudo-binary system SiO_2–MgO, R decreases from 1 for pure SiO_2 to 0·2 for 60% of MgO; this must result in a lower vaporization. The influence of Al_2O_3 is important. Introducing MgO in SiO_2–Al_2O_3 leads to a minimum in R as long as the Al_2O_3 content does not reach 60%, i. e. as long as the biphased slag–mullite domain exists. The minimum value is slightly decreased with the Al_2O_3 content. With such trends and considering the physical properties of the phases involved it could be interesting to:

(i) Select compositions allowing (above 1870K) the biphased domain liquid-mullite to be reached; the viscous glass will enable stress accommodation, the solid phase exhibiting a lower oxygen diffusion coefficient than the liquid one and a low thermal expansion coefficient in front of the parent oxides.
(ii) Introduce MgO contents close to the cordierite composition; in this region, zero or very low thermal expansion coefficient glasses are present, and they exhibit good thermal shock resistances. Furthermore the possibility to obtain a glass (non-equilibrium state) suggests that such a layer could protect at temperatures lower than those defined by the liquidus.

In summary the calculations show the influence of an ‘alloyed silica’, as long as it also exhibits a low reactivity with the SiC underlayer.

4.2 Behaviour of the system Si–Al–Mg–O–C

Equilibrium calculations were developed in the same way as in the previous section. The aim was to investigate the behaviour between SiC and a

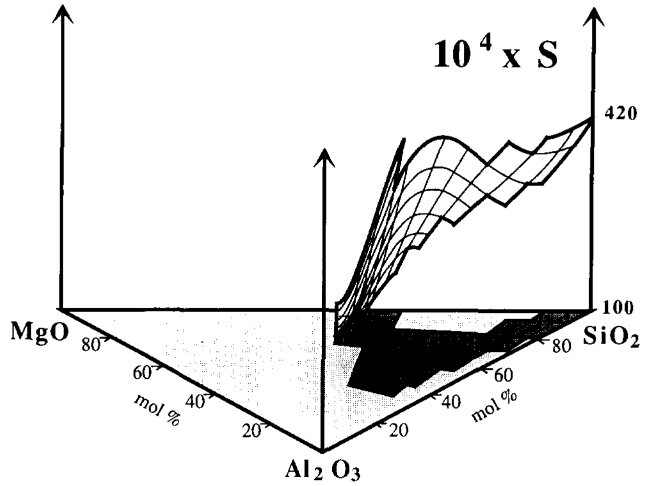

Fig. 5. Silicon 'solubility' in the gas phase (S ratio) connected with the interaction of SiC and a ternary liquid phase at 2000 K.

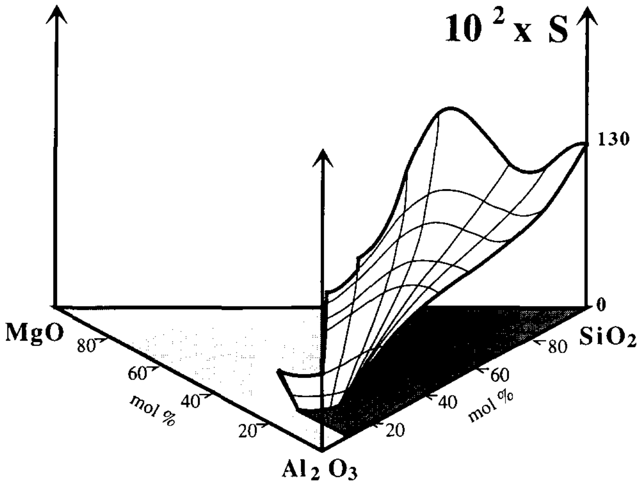

Fig. 6. Silicon 'solubility' in the gas phase (S ratio) connected with the interaction of SiC and a ternary liquid phase at 2250 K.

ternary oxide melt compared to what happens in the system Si–O–C (that is between SiC and SiO_2).

In order to simulate the interaction phenomenon, the SiC phase must remain; then it is always introduced in a large amount compared to oxygen: 10 moles of SiC and 1 mole of O_2. Such an input ratio must lead to equilibrium compositions where SiC exists with the other condensed phases. The influence of increasing Al_2O_3 and MgO amounts was tested for two constant temperatures (T = 2000 K and T = 2250 K) in a closed vessel (constant volume). In this way an equilibrium between a slag, SiC and the gas phase was obtained. In the latter the main species were CO(g), SiO(g) but also gaseous oxide products and Mg(g) when a large input of MgO was considered. To clearly characterize the high temperature behaviour of this system, the partial pressure of silicon monoxide SiO(g) may be used to reflect the stability of the condensed phases. As for all calculations, the input silicon is constant, the variations can be represented by the ratio S defined as the silicon amount in the gas phase to the silicon present in the liquid phase, that is some kind of 'solubility' expressed simply by $S = n_1$ SiO(g)/n_2 SiO_2(slag). Typical results are shown in Figs 5 and 6 which need some comments. S is calculated and represented only over the liquid single-phase field in the pseudo-ternary system. Outside these boundaries a biphased field (slag + solid oxide phase) is obtained and the SiO(g) amount does not vary any more. It has to be mentioned that at 2000K, some points in relation with the pseudo-binary SiO_2–MgO were discarded as the modelization is unable to take into account a separation phenomenon.

S varies strongly; it decreases when the Al_2O_3 content increases. An addition of MgO enhances this behaviour: the effects may be regarded as cumulative. Examination of the components in the gas phase reveals that in all the cases the equilibrium mole numbers of SiO(g) and CO(g) are in a constant ratio (very close to 2). So S is a fairly good representation of the reactivity between SiC and more or less complex oxides melts.

From the figures it may be deduced that the slag is more efficient at the highest temperature since the ordinate varies a hundredfold instead of fourfold at 2000 K.

Conclusion

In summary, with respect to the applied goal of protection against oxygen at high temperature, the thermodynamic studies allow the proposal of a way to protect carbon–carbon composites. Such a protection could be constituted of a SiC layer coated by a mixture, SiO_2–Al_2O_3 or SiO_2–Al_2O_3–MgO. The calculations in an equilibrium system indicate that the reactivity is theoretically reduced with regard to pure SiO_2, but it remains to be seen whether the real system is not too far from equilibrium.

From a technological point of view, such an outer oxide layer can be obtained by direct techniques: enamelling, sol–gel, plasma torch, or indirect ones such as chemical vapour deposition. In this latter case, pure Al_2O_3 could be deposited on SiC and the binary slag would be obtained during the first firing in an oxidative atmosphere. Furthermore, such an approach is useful to identify some solutions or new concepts. Other pseudo-binary systems such as the SiO_2–ZrO_2 would behave similarly and could be of interest for further research at high temperature.

Acknowledgements

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