Interfacial chemistry: Reactions in inorganic systems

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Abstract: The use of equilibrium thermodynamics in describing interfacial reactions in inorganic systems is demonstrated using examples of interactions between non-oxide materials (C, Si, SiC, Si_3N_4) and transition metals (Ti, Mo, Pt).

In the case of diffusion-controlled process, solid-state reactions can be interpreted with chemical potenial diagrams. However, in some cases a periodic layered morphology is found in the reaction zone, which is not fully understood and it is difficult to predict a priori. The interfacial phenomena in systems based on dense Si_3N_4 and non-nitride forming metals can be explained by assuming a nitrogen pressure build-up at the contact surface. This pressure determines the chemical potential of Si at the interface and, hence, the reaction products formed in the diffusion zone.

Traces of oxygen in the ambient atmosphere might affect the interaction at the interfaces. This is especially of importance when both members of the diffusion couple can form gaseous products. The thermodynamic stability of the condensed phases in the systems where volatile species may form can be described using predominance-type thermochemical diagrams.

INTRODUCTION

Interfacial phenomena are of concern in a wide variety of multiphase inorganic systems which include composite materials, coatings, bonded components, thin-film electronic devices etc. In this paper we are going to disucss some chemical aspects which may affect, or even control, the morphological evolution of the interfacial region between inorganic materials at elevated temperatures. An attempt is made to identify the present state of knowledge about interfacial microchemistry. Interaction at the interfaces will be analysed in terms of whether new phases or solid solutions are formed.

When a chemical reaction between two dissimilar materials occurs, the nucleation of new phases takes place at the interfaces, along with the associated mass transfer. The chemical interaction is governed by the thermodynamics and reaction kinetics of the system under consideration. The former dictates which phases are stable at the processing and service conditions and the latter determines how much of a phase can be formed.

In the treatment that follows, kinetic barriers for nucleation are neglected and local thermodynamic equilibria are assumed at the interface vicinity. This implies that the chemical potentials (activites) of various species change continuously within a phase layer and have the same value at both sides of interphase interface. Especially at an early stage of interaction this is not always true, for instance, in thin-film experiments the interface composition does not always match the equilibrium phase diagram value. Interface energies play an important part in that case, and amorphisation phenomena can

occur. However, we will not go into these interesting aspects and just suppose that volume diffusion in a system is the rate-limiting step and only the equilibrium crystalline phases are formed.

The present discussion is confined to the chemical interactions in a few systems involving non-oxide inorganic materials (C, Si, SiC, Si_3N_4) and transition metals (Ti, Pt, Mo).

ANALYSIS OF INTERFACIAL REACTIONS USING CHEMICAL POTENTIAL DIAGRAMS

In this part of the discussion we will demonstrate the use of a combined equilibrium thermodyamic and diffusion kinetic approach in predicting the variation of chemical composition in the diffusion zone during solid state reactions between SiC and transition metals (Mo, Ti). Emphasis is placed primarily on metal/ceramic interfaces formed during diffusion bonding or by a CVD-process.

Contrary to binary systems it is possible in a ternary system to develop two-phase areas in the diffusion zone because of the extra degree of freedom. The diffusion path, the locus of the average composition in the interaction zone, reflects the morphology of the reaction zone. If phases are separated by planar interfaces, the diffusion path crosses the two-phase region parallel to a tie-line, and along the whole interface the same local equilibrium can be assumed. However, this is not necessarily the case; regions of supersaturation can be formed near the interfaces. This implies an interface which is thermodynamically unstable and gives rise to wavy interfaces or isolated precipitates. The diffusion path then crosses the tie-lines in the two-phase fields.

Rapp et.al. (ref. 1) developed a simple model to predict the morphological evolution of the diffusion zone during solid-solid displacement reactions based on the criterion of the limiting diffusion step in the product layers. Van Loo (ref. 2) introduced an aditional guiding rule, stating that the *intrinsic* diffusion of an element takes place only in a direction in which the chemical potential (activity) of that element decreases.

Let us consider, as an example, solid state interaction at the interface between Mo and SiC deposited by the CVD-process. The isothermal cross-section through the ternary Mo-Si-C phase diagram at 1473 K is given in Fig. 1a (ref. 3). The presence of the ternary carbosilicide Mo_5Si_3C in equilibrium with all carbon-containing phases (C, Mo_2C, SiC) entirely determines the topology of the diagram. The equilibrium diagram provides the framework for understanding interfacial reactions in the Mo/SiC system. However, from this cross-section alone it is not unambiguously clear how the resulting microstructure of the reaction zone will evolve. A diffusion path such as $SiC/Mo_5Si_3/Mo_5Si_3C/Mo_2C/Mo_3Si/Mo$, for example, can not be excluded when looking only at the experimentally determined phase equilibria in the system. In principle, all neighbouring phases in this hypothetical diffusion couple can coexist in equilibrium and mass balance can be preserved.

As mentioned earlier, for a diffusion-controlled process the thermodynamic activity of species varies continuously through the reaction zone. The concentration of each component, however, may change discontinuously and even "up-hill" across phase boundaries from one end-member of a diffusion couple to the other. Since intrinsic fluxes of atoms in the reaction zone are controlled by the direction and magnitude of chemical potential gradients, the nature of the diffusion phenomena can be better interpreted by superimposing the diffusion path on the potential diagram rather than on the Gibbs composition triangle. The utilazation of this approach has already been demonstrated on examples of many inorganic systems (ref. 4,5).

a)   b)
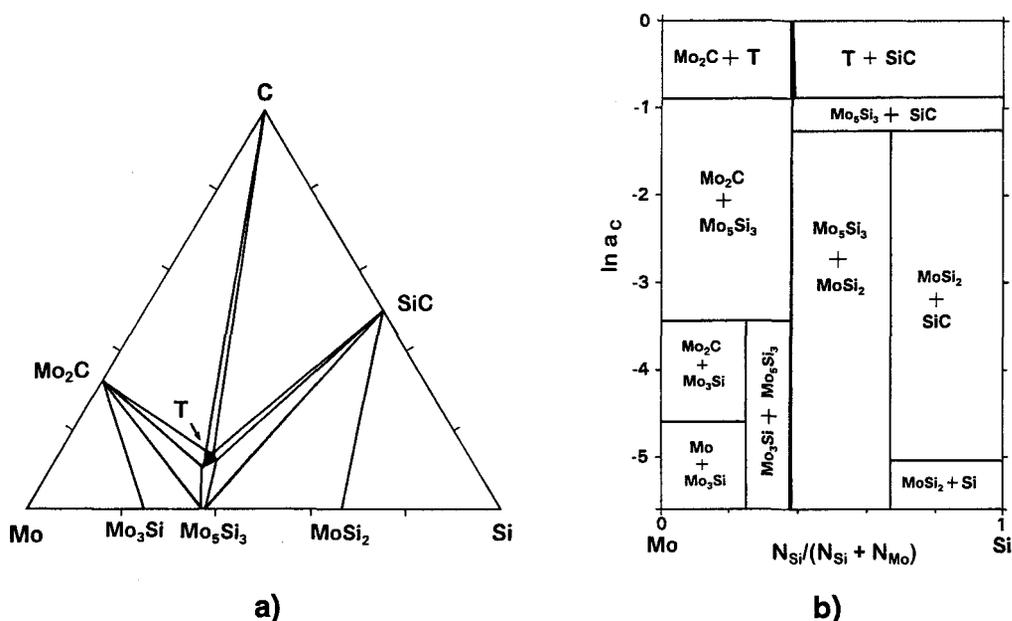
Fig. 1 a) Experimentally determined isothermal cross-section through the Mo-Si-C phase diagram at 1473; b) corresponding potential (activity) diagram for carbon (T=Mo_5Si_3C).

The potential diagram for carbon, the species which has to diffuse intrinsically in the proposed sequence from the left-hand to the right-hand side, can readily be calculated using pertinent thermodynamic information on the Mo-Si-C system (Fig. 1b). It can be seen that the ternary phase Mo_5Si_3C can never be formed in the diffusion zone at the position given above, since the intrinsic diffusion of carbon should then take place through Mo_5Si_3 towards a higher activity which is thermodynamically forbidden. In fact, this model can be used in order to predict the layer sequences which are not allowed.

Experimentally, a continuous layer of the ternary phase Mo_5Si_3C was found next to SiC in the transition zone of the diffusion couple Mo/SiC, after annealing at 1473 K in vacuum. Then, the diffusion path crosses the tie-lines in the two-phase region $Mo_5Si_3+Mo_2C$ resulting in the formation of an interwoven reaction layer. Eventually, the reaction path proceeds in the phase sequence $SiC/Mo_5Si_3C/Mo_5Si_3+Mo_2C/Mo_2C/Mo$ which is indeed kinetically allowed and thermodynamically possible as may be concluded from the isothermal section and potential diagram.

Formation of the ternary compound in contact with SiC could be expected when using the consideration of Chang et al. (ref. 6). They state that, at the initial stages of interaction, the overall composition near the interface should be very close to the mass balance line. This implies that the first nucleated phase at the metal/SiC interface is expected to be the ternary compound. In other words, the phase consisting of three elements has a better chance to form in a ternary diffusion couple.

However, in the Ti/SiC system the ternary phase Ti_3SiC_2 which has been reported (ref. 7) was not identified inside the diffusion zone in our latest experiments when hot isostatically pressed SiC-ceramic (HIPSiC) and/or 6H SiC single crystals were used as end-members. Instead, a mixed reaction layer is formed (Fig. 2a). This layer consists of $Ti_5Si_3(C)$ and titanium carbide. However, according to the phase diagram Fig. 2b (ref. 8), $Ti_5Si_3(C)$ cannot be in equilibrium with SiC. Probably a (very thin) layer of titanium carbide or Ti_3SiC_2 is present at the interface with SiC which we could not detect. The diffusion-activity model shows that the diffusion paths without Ti-
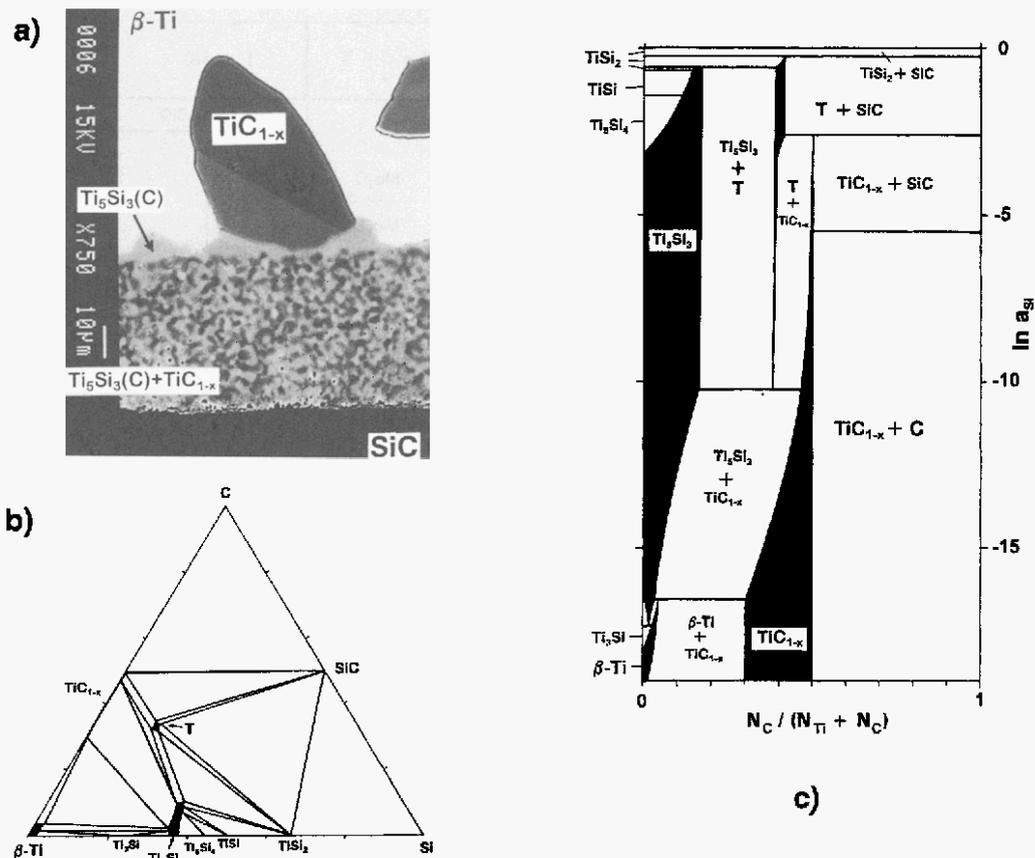
Fig. 2 a) Back-scattered electron image (BEI) of the diffusion zone between HIPSiC and Ti after annealing at 1373 K for 196 hr in vacuum; b) experimentally determined isothermal cross-section through the Ti-Si-C phase diagram at 1373 K (T=Ti$_3$SiC$_2$); c) potential diagram for silicon in the Ti-Si-C system at 1373 K.

carbosilicide formation are possible. For example, a reaction path, like SiC/TiC$_{1-x}$/Ti$_5$Si$_3$(C)+TiC$_{1-x}$ / Ti$_5$Si$_3$(C)/β-Ti can be justified using the potential diagram (Fig. 2c). One might expect that the reaction between metal and SiC can be changed by using SiC with excess of Si or C. The prevailing silicon or carbon activity at the metal/ceramic interface controls the phase formation of either Ti$_3$SiC$_2$ or TiC$_{1-x}$. The phase formation,therefore, can be very sensitive to the stoichiometry and impurity content in the initial materials. Moreover, silicon carbide has a very low stacking fault energy which can allow solid state transformation and formation of many different polytypes even during growth of single crystals. This might also account for the differences given by various research groups studying interfacial reactions in SiC/Ti system (ref. 7,9).

In the case of reactions of non-carbide forming metals with SiC no thermodynamically stable carbides or carbosilicides are present. Only carbon can be formed as a side product next to the metal silicides or metal-silicon solid solution. The behaviour of carbon formed by the interfacial reaction determines largely the microstructural evolution of the diffusion zone.

SOLID STATE REACTIONS OF SiC WITH NON-CARBIDE FORMING METALS; PERIODIC LAYER FORMATION

The ternary system Pt-SiC is considered as an example. It is possible to predict the phase sequence in the reaction zone using just the isothermal cross-section through the Pt-Si-C phase diagram (Fig. 3a). In graphite the thermodyanmic activity of carbon is one and in SiC lower than one. It is, therefore, impossible that the carbon formed by the interfacial reaction will diffuse through the

a)

b)
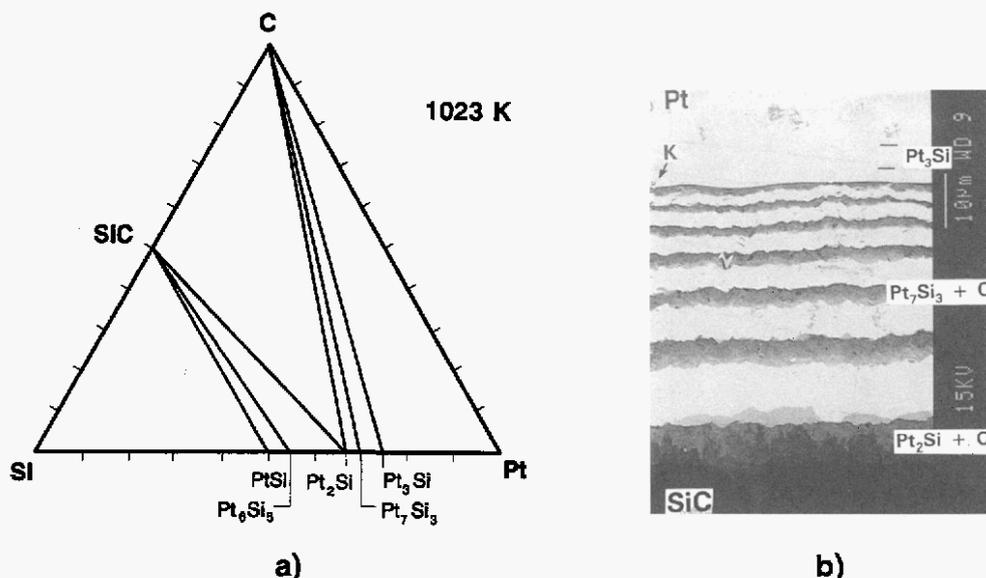
Fig. 3 a) Isothermal section through the phase diagram Pt-Si-C and b) morphology (BEI) of the reaction zone in Pt/HIPSiC diffusion couple (1023 K; 16 hr, vacuum).

reaction zone towards a graphite phase at the metal side, because it would then have to diffuse against the gradient of its chemical potential. Thus the graphite will stay next to the SiC. The most Si-rich silicide next to the graphite is the one that is involved in the monovariant equilibrium silicide + SiC + C. Experimentally however, carbon was found in the transition zone in the form of the regular bands through the silicide layer parallel to the original interface (Fig. 3b). The bands consist of graphite particles imbedded in a continuous intermetallic matrix phase. A clear periodic structure of graphite particles in a matrix of the Pt_7Si_3 is visible in a Pt/SiC couple annealed at 1023 K. Also, the formation of a continuous two-phase layer (Pt_2Si+C) next to the SiC/reaction zone interface was found. The Kirkendall plane is located in the Pt_7Si_3 phase close to the Pt_7Si_3/Pt_3Si interface. This proves that Pt is the most mobile species in Pt_7Si_3. The band formation stopes when the Pt_2Si phase grows to a thickness where the Pt_2Si/Pt_7Si_3 interface is located outside the carbon-containing zone (ref.10).

The periodic pattern formation in this system is understood as a manifestation of the Kirkendall effect (ref. 11). In a more general way, the mechanism is operative when the components have widely different mobilities in adjacent phases. Using a "multi-foil" diffusion couple technique it was shown that at 1023 K the mobility of Si is higher than that of Pt inside Pt_2Si (ref. 10). The Pt_2Si/Pt_7Si_3 interface must, therefore, be a source of vacancies (ref. 12). There is a large flux of vacancies from the interface in the direction of Pt and a small flux in the direction of SiC. As long as the inert graphite particles remain inside Pt_2Si they will experience a Kirkendall force in the direction of SiC. In the Pt_7Si_3 phase, however, they move into the direction of Pt. These opposing forces will eventually "split-up" the carbon band at (or in the vicinity of) the Pt_2Si/Pt_7Si_3 interface. After this "splitting" the process will repeat.

The appearance of a periodic layered reaction zone during solid state interaction seems to be a general diffusion phenomenon. The formation of spatiotemporal patterns was found in other systems like: Ni/SiC (ref. 13), Fe_3Si/Zn (ref. 14), Co_2Si/Zn (ref. 15), Ni_3Si_2/Zn, $Ni_{50}Co_{20}Fe_{30}/Mg$ (ref. 16).

INTERFACIAL REACTIONS IN WHICH A VOLATILE PRODUCT IS FORMED

Now we shall take a closer look at some aspects of interactions between Si_3N_4 and metals. The simplest situation occurs when a nitride forming metal (e.g. Ti) reacts with Si_3N_4-ceramic at elevated
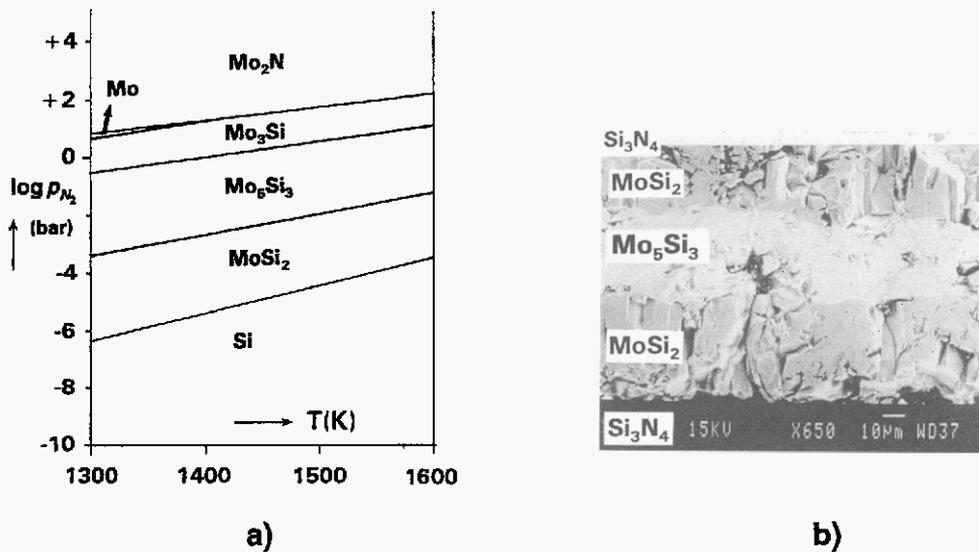
Fig. 4 a) Stability diagram showing solid phases in equilibrium with solid Si₃N₄ in the Mo-Si-N system as a function
of temperature and nitrogen partial pressure (fugacity); b) secondary electron image of the reaction zone between Mo
and 50 % porous Si₃N₄ annealed 50 hr at 1573 K in vacuum..

temperatures and the partial pressure of nitrogen in an ambient environment is higher than the
dissociation pressure of silicon nitride. In this case the general ideas of the preceeding sections can
be applied and interfacial reactions can be interpreted using the potential diagrams (ref. 17).

In the reaction of Si₃N₄ with a non-nitride forming metal, however, the product will be one or more
metal silicides (or solid solution) plus nitrogen gas. This nitrogen gas has to disappear from the
interface and it is clear that this poses some problems. The type of reaction products which can be
formed at an elevated temperature in the diffusion zone between Si₃N₄ and any metal (or alloy)
depends on the chemical potential (activity) of silicon and, hence on the activity (fugacity) of
nitrogen at the contact surface. When using diffusion couples consisting of dense Si₃N₄ ceramic and
non-nitride forming metal, the interior of the couple is not in direct contact with the surrounding
atmosphere. Nitrogen which is formed by the interfacial reaction cannot escape easily. A nitrogen
pressure (fugacity) will build up at the contact surface. This pressure determines the activity of Si at
the metal/ceramic interface. It is clear that in such a system the partial pressure of nitrogen (and
therefore its chemical activity) can cover a large range of values. The isothermal cross-section
through the phase diagram Me-Si-N and, more specifically, the position of the monovariant
equilibrium N_2-gas + Si_3N_4 + Me_xSi_y is dependent on this partial pressure.

The calculated stability diagram for the Mo-Si-N system is given as an example in Fig. 4a (ref. 18).
This graph displays which solid phases of the sytem are in equilibrium with Si₃N₄ as a function of
temperature and partial pressure of nitrogen. The thermodynamic activity of silicon at the
metal/ceramic interface is realted to the N₂ partial pressure through the equilibrium constant of
Si₃N₄. Only Mo₃Si was found in the reaction zone after diffusion bonding of dense Si₃N₄ with Mo at
1573 K in vacuum and no Mo₂N had been formed. According to calculations it means that the
nitrogen pressure at the interface can be estimated to be somewhere in between 10 and 100 bar. This
is corroborated by the diffusion couple experiment between Mo and 50 % porous Si₃N₄ (Fig. 4b).
Layers consisting of MoSi₂ and Mo₅Si₃ are formed in the transition zone. Obviously, the whole Mo
part of the couple has been consumed, as well as the Mo₃Si layer which must have been present after
shorter annealing times. It is clear that no N₂ pressure can build up at the interface because nitrogen
can escape through the open pores in the Si₃N₄. It increases the chemical potential of Si at the
contact surface resulting in the formation Si-rich silicides. In other words, the reaction products in
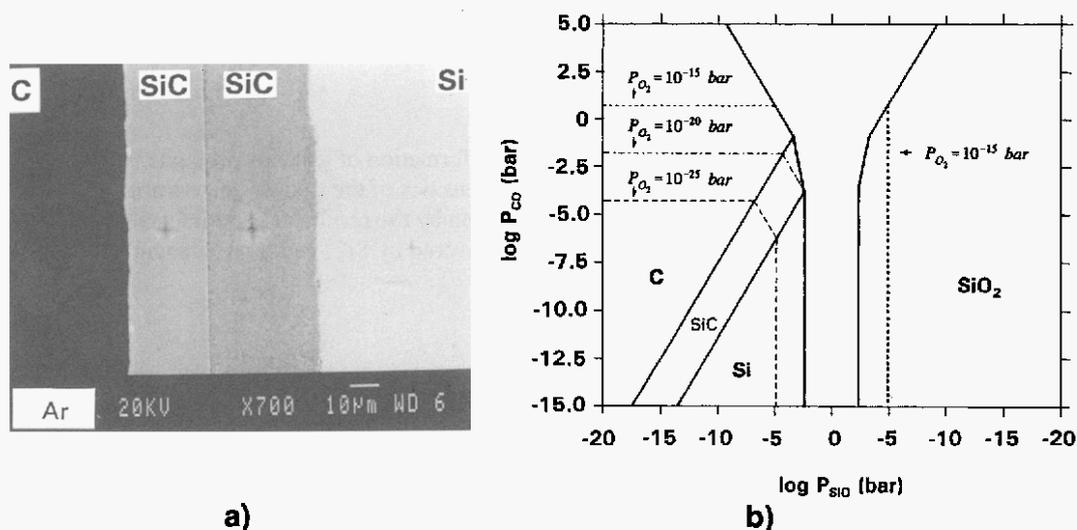
Fig. 5 a) BEI of the reaction zone between Si and C after annealing at 1623 K for 72 hr in argon; b) a Si-C-O predominance diagram at 1623 K.

this couple will entirely depend on the surrounding N_2-partial pressure, because this pressure determines the activity of Si at S_3N_4 interface.

A nitrogen pressure build-up at the metal/ceramic interface is also proven experimentally by studying the interfacial reactions in Ni/Si_3N_4 (ref. 18), Ni,Cr/Si_3N_4 (ref. 19) and Fe/Si_3N_4 (ref. 20) systems.

Obviously, the microstructural development of the transition zone between dissimilar materials can be even more intricate when under the circumstances of the experiment both end-members of a diffusion couple can form gaseous products. This can be demonstrated by the high temperature interaction at the contact surface between carbon and silicion when the ambient atmosphere contains small amounts of oxygen (e.g. under Ar with $Po_2 \approx 10^{-4}$ bar) (ref. 21).

The formation of two distinct layers of SiC is observed in the transition zone between glassy carbon and Si after annealing at 1623 K in argon (fig. 5a). The layer on the C side has a Vickers microhardness $HV \approx 1100$, compared to $HV \approx 400$ on the Si side and $HV \approx 3900$ for dense HIPSiC. This indicates that both layers are porous, with the higher porosity on the Si side. It was also found that SiC is formed on the outside of the couple halves, showing that gas-solid reactions are responsible for the formation.

In general, the thermodynamic phase stability for the condensed phases in systems where volatile species may form can be described by high temperature Pourbaix-type diagrams, and these can be used to interpret gas-solid interactions. Such a predominance diagram for Si-C-O system at 1623 K is given in Fig. 5b. In this construction we have chosen P_{SiO} and P_{CO} as the independent variables. The Ar gas used in our experiments exhibits a partial oxygen pressure of about 10^{-4} bar. Under these conditions the possible reactions are:

$$2C_{(s)} + O_{2(g)} = 2CO_{(g)} \tag{1}$$
$$Si_{(s)} + O_{2(g)} = SiO_{2(s)} \tag{2}$$
$$SiO_{2(s)} + Si_{(s)} = 2SiO_{(g)} \tag{3}$$
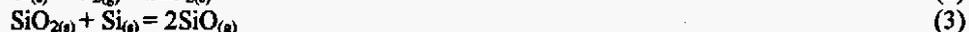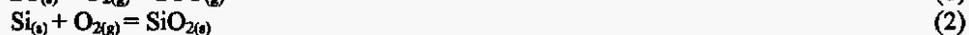
The region on the diagram where $P_{SiO} > 2 \cdot 10^{-4}$ bar and $P_{CO} > 2 \cdot 10^{-4}$ bar cannot be attained under our experimental conditions: the central part in this figure does not exist under equilibrium conditions.

After formation of SiO and CO silicon carbide is formed on the two couple halves, according to reactions:

$$2C_{(s)} + SiO_{(g)} = CO_{(g)} + SiC_{(s)} \tag{4}$$
$$2Si_{(s)} + CO_{(g)} = SiO_{(g)} + SiC_{(s)} \tag{5}$$
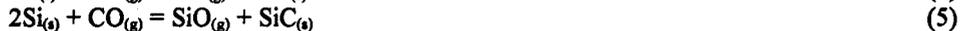
The porosity of the product SiC-layer can be attributed to the formation of gaseous products in reactions (4) and (5). However, we cannot explain why the densities of the two SiC layers are different. The contribution of gas phase transport is also proven by the results of experiments where Si and C were separated by spacers and both C and Si were covered by SiC, and by examining equilibrated powder compacts C+Si and C+SiO$_2$.

CONCLUDING REMARKS

The interfacial phenomena in inorganic materials systems can obviously be quite complex. However, by using pertinent thermodynamic data (phase diagrams and potential diagrams) one often can predict the composition of the diffusion zone.

Many problems remain, for example the role of mechanical stresses which result from the diffusion process. Also the role of interface energies and non-equilibrium situations, which have not been discussed here, pose some questions, in particular at the initial stages of the interaction.

Apart from these problems, the ambient atmosphere may also influence the reaction products, expecially where high-temperature interactions between non-oxide inorganic materials are concerned.

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