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REACTIONS IN THE SYSTEMS Mo–Si₃N₄ AND Ni–Si₃N₄

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Laboratory of Solid State Chemistry and Materials Science, Centre for Technical Ceramics CTK, Eindhoven University of Technology, The Netherlands

Abstract—The reaction products, formed during annealing of porous powder mixtures of Si₃N₄ with non-nitride forming metals like Ni or Mo, will depend on the partial pressure of N₂ in the atmosphere. In a diffusion couple, however, nitrogen has to be released at the Si₃N₄-interface during the formation of a metal silicide. It cannot escape easily and builds up a higher pressure of nitrogen at this interface. Therefore, the reaction products are different from those in porous pellets. This has been verified for Ni–Si₃N₄ and Mo–Si₃N₄ couples. The role of traces of oxygen on these reactions will be discussed.

Résumé—Les produits de réaction formés pendant le recuit de mélange de poudres poreuses de Si₃N₄ avec des métaux qui ne forment pas de nitrures tels que Ni ou Mo, dépendent de la pression partielle de N₂ dans l'atmosphère. Cependant, dans un couple de diffusion de l'azote doit être libéré à l'interface de Si₃N₄ pendant la formation d'un silicid métallique. Il ne peut pas s'échapper facilement et produit une pression d'azote plus élevée à cette interface. Donc, les produits de la réaction sont différents de ceux des pastilles poreuses. Ceci a été vérifié pour les couples Ni–Si₃N₄ et Mo–Si₃N₄. Le rôle de traces d'oxygène dans ces réactions est aussi discuté.


1. INTRODUCTION

When metals and ceramics are in contact with each other at high temperature, chemical reactions will often take place, leading to new phases. Sometimes only solid solutions will develop by diffusion of constituents from the ceramic in the metal. Often the isothermal cross-section through the phase diagram allows us to predict what actually will happen in such a system if thermodynamic equilibrium at the interfaces is assumed; however the relative mobilities may also be of importance. The role of thermodynamics (phase diagram) and kinetics (diffusion rate) will be discussed in a few examples.

First, consider an isothermal phase diagram of the type shown in Fig. 1. A solid solution of the atoms from the ceramic BC in the metal A can exist in equilibrium with the compounds AC and BC. From the isotherm it can be seen that, if a planar slice of pure A is brought in contact with a planar slice of ceramic BC as a so-called infinite diffusion couple, a solid solution must be formed. Whether or not also the compound AC will be formed depends on the relative diffusivities of B and C in the metal A. If, like in Fig. 1(a), C-atoms diffuse faster than B-atoms, they will penetrate further into the bulk of slice A. The diffusion path, defined as the locus of the average composition found in the diffusion couple parallel to the original interface, will therefore start from A in the direction C. At a certain point, closer to the interface, B atoms are also present and the diffusion path will turn towards the B-corner of the isotherm. From mass balance considerations the total number of B and C atoms which left the stoichiometric ceramic BC must be equal and the diffusion path must cross the line connecting A and BC. The expected diffusion path, shown in Fig. 1(a), therefore predicts in this couple only the formation of a solid solution of B and C in A. If, however, the mobility of B atoms in A is higher than the mobility of C atoms, the diffusion path will start from A in the direction of B, as shown in Fig. 1(b). Again, according to the mass balance, the path must cross the line from A to BC and will enter the two-phase region A/AC. The phase AC can be formed as a layer parallel to the interface as depicted by the diffusion path in Fig. 1(b), or as precipitates in the A-matrix. It is even possible that the pure element C will be formed. These alternatives can be predicted if one knows the diffusivities of all elements in the phases A
Fig. 1. The diffusion path (dotted line) in a diffusion couple between A and BC (a, b) and between a solid solution A$_{1-x}$C$_x$ and BC (c). The dashed line is the connection line between the two end members of the couple. In (a, c) the diffusivity of C atoms is larger than that of B atoms in the A-phase; in (b) B-atoms are supposed to be faster diffusing than C-atoms.

and AC [1]. Qualitative knowledge, in the sense of knowing the sequence in diffusion rate of the elements in these phases, is often enough to predict the product sequence and morphology in a diffusion couple [2-4].

It can also be seen from the magnified A-corner of the isotherm in Fig. 1(c) that, starting the diffusion experiment not with pure A but with A$_{1-x}$C$_x$, a solid solution of C in A, the compound AC can be formed even if C atoms diffuse faster than B atoms in A. In the system Ni–Al$_2$O$_3$ situations like the one depicted in Fig. 1(a, c) have actually been found [4, 5].

In a second example, schematically shown in Fig. 2 and experimentally encountered in e.g. the systems Fe–SiC or Ni–SiC [6, 7], the predictions are much easier to make since the phase diagram completely predicts the phases which will develop in a couple A/BC. It is assumed that phases which are formed in contact with each other in a diffusion couple should be in equilibrium. Therefore, sequences like A/A$_3$B/AB/AB$_3$/C/BC are forbidden since C is not in equilibrium with the compound AB$_3$. But a sequence like A/A$_3$B/C/AB/AB$_3$/BC is also forbidden, although all phases can coexist in equilibrium. The reason is that the element C should then intrinsically diffuse from BC, through AB$_3$ with a chemical activity of C smaller than one, to pure C with a chemical activity equal to one. This is thermodynamically forbidden: only if the diffusion equations are presented in a Matano-type frame of reference can the resulting interdiffusion fluxes show an up-hill activity character. Intrinsic fluxes, which represent real atom jumps from one lattice site to another, can only proceed in a direction of decreasing chemical activity [3]. Therefore, only the sequence A/A$_3$B/AB/C/BC is possible.

Fig. 2. A fictitious phase diagram of the system A–B–C in which all phases are considered as line compounds.
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from a thermodynamic point of view. In reality this is indeed found in the Fe–SiC and Ni–SiC systems, although there the element C (carbon) gets dispersed in the intermetallic compounds during the diffusion process. Carbon is, however, indeed not found in contact with the pure elements Fe or Ni [6].

In this article we will discuss in more detail reaction phenomena in the systems Mo–Si₃N₄ and Ni–Si₃N₄. The interesting point in the systems containing a gas phase like N₂ is the dependence of the phase diagram upon the total pressure and, especially, the partial pressure of N₂. Therefore, we can create various isothermal cross-sections at one fixed temperature by varying the N₂ partial pressure. This gives an ideal possibility to verify theoretical predictions concerning the phases formed during reaction between Mo or Ni and Si₃N₄. Apart from that it will be clear that in joining technology as well as for the behaviour of coatings and composite materials with Si₃N₄ as a component, understanding of these reactions is important. We will show that the reaction behaviour can indeed be predicted but also that traces of oxygen, present at the ceramic surface or in the gas atmosphere, may play an important role. These
Table 1. Partial pressure of N$_2$[bar] above equilibrated mixtures of two or three solid phases at 1573 K according to the thermodynamic data given by Refs [9, 10]

<table>
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<tbody>
<tr>
<td>Si-MoSi$_2$-N$_2$</td>
<td>&lt;1.8 x 10$^{-4}$</td>
<td>&lt;1.8 x 10$^{-4}$</td>
</tr>
<tr>
<td>Si-MoSi$_2$-Si$_3$N$_4$</td>
<td>1.8 x 10$^{-4}$</td>
<td>1.8 x 10$^{-4}$</td>
</tr>
<tr>
<td>Mo$_3$Si$_2$-Mo$_2$Si$_3$-Si$_3$N$_4$</td>
<td>0.03</td>
<td>0.18</td>
</tr>
<tr>
<td>Mo$_3$Si$_2$-Mo$_2$N</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>Mo$_3$Si$_2$-Mo$_2$Si$_3$-Mo$_2$N</td>
<td>88</td>
<td>88</td>
</tr>
<tr>
<td>Mo$_3$Si$_2$-Mo$_2$N-Si$_3$N$_4$</td>
<td>98</td>
<td>212</td>
</tr>
<tr>
<td>Mo$_3$Si$_2$-Ni$_3$N$_4$-N$_2$</td>
<td>98</td>
<td>212</td>
</tr>
</tbody>
</table>

predictions lead to useful strategies for improving bonding.

2. EXPERIMENTAL

The Mo-foils used for preparing the diffusion couples are of various dimensions (ranging in thickness from 0.05 to 0.12 mm) with a purity of 99.95%. The Ni-slices vary between 0.1 and 1 mm thickness with a purity of 99.98%. Si$_3$N$_4$ has been used in various qualities because of the possible importance of the presence of sintering additives and porosity. We will report here on dense ESK-HP-Si$_3$N$_4$ with 1.5 wt% MgO, dense HP-Si$_3$N$_4$ with 5 wt% Y$_2$O$_3$ + 1 wt% Al$_2$O$_3$ and porous Si$_3$N$_4$ without intentional additives, prepared in our own laboratory from Si$_3$N$_4$-powder (~t/a+f195%, purity 98.2 wt%), sintered to 50% density.

For verifying the isothermal cross-sections of the phase diagrams we have prepared a number of powder mixtures of Mo or Ni (99.98) and Si$_3$N$_4$, which have been cold-pressed into a pellet and then annealed.

The annealing of the diffusion couples and pellets has mostly taken place at 1573 K (1300°C) for Mo-Si$_3$N$_4$ and 1373 K (1100°C) for Ni-Si$_3$N$_4$ under various conditions. For total gas pressures up to 100 bar (10$^7$ Pa) a special sintering furnace has been used; an external load of 2 MPa is used to join the Si$_3$N$_4$-metal-Si$_3$N$_4$ sandwich couples. For vacuum conditions with a residual pressure of 6 x 10$^{-5}$ Pa electron-gun furnaces have been used, designed in our laboratory and described elsewhere [8]. Also here, the sandwich couples are joined by an external load of 2 MPa. For conditions in flowing gas of one bar pressure, horizontal tube furnaces have been used. The diffusion couples are then pressed together by a spring situated outside the hot part of the furnace which exerts a load of about 10 MPa through Al$_2$O$_3$ tubes.

After annealing and metallographic preparation, the couples and pellets have been examined by optical microscopy, X-ray diffraction, scanning electron microscopy and electron probe micro analysis.

Apart from experiments we have also performed calculations. Using Refs [9, 10] for the Gibbs energy of formation for the Mo–Si compounds and the nearly equal value given in Refs [8, 11, 12] of $-224.7$ kJ/mol for the $\Delta G^f$ of Si$_3$N$_4$, the isothermal section at 1573 K through the Mo–Si–N phase diagram can be calculated as a function of the partial pressure of nitrogen. For the Ni–Si–N system a number of isothermal sections at 1373 K have been calculated. The thermodynamic data on the Ni–Si system have been estimated in our laboratory [7]. Literature values found in Refs [9, 13, 14] were not consistent with some experimental facts found in the Ni-SiC system [7]. Also calculations are made for stability diagrams of the solid phases in the Si–N–O system as a function of the partial pressure of N$_2$ and O$_2$ at 1373 and 1573 K, using data from Heuer and Lou [11].

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. Powder experiments

Using the Gibbs energy values of Barin and Knacke [9] for the various compounds, the isothermal sections through the Mo–Si–N diagram as a function of the N$_2$ partial pressure are shown in Fig. 3. If the $\Delta G^f$-values from Vahlas et al. [10] are used for the Mo-silicides, the sequence of the diagram remains the same but the absolute values of the N$_2$ partial pressure differ somewhat as shown in Table 1.

Table 1 must be read in the way that e.g. at partial pressures of nitrogen between 0.03 and 7 bar, Si$_3$N$_4$ is in equilibrium with Mo$_3$Si$_2$ according to the thermodynamic data of Barin and Knacke [9].

The same information about the phases which are in equilibrium with Si$_3$N$_4$ can be found by examining Fig. 4. This plot can easily be made by performing the former calculations at various temperatures. The phase diagrams of Fig. 3 can be found along the dashed line at 1573 K [except Fig. 3(e) in which the same phases are in equilibrium with Si$_3$N$_4$ as in Fig. 3(d)].
Our experimental results on sintered Mo–Si powder pellets generally agree with the predictions shown in Figs 3 and 4, as shown in Table 2. The powder mixtures are depicted as points in the phase diagrams of Fig. 3. The experiments at $p_{N_2} = 100$ bar suggest that the value of the Gibbs energy of formation for Mo$_3$Si from Ref. [9] is more accurate than in Ref. [10].

For the Ni–Si–N system powder experiments are performed at $N_2$ pressures up to 1 bar. The calculated stability plots of the Ni-silicide phases in equilibrium with both Si$_3$N$_4$ and $N_2$ are shown in Fig. 5(a,b). These plots are to be considered as preliminary, since the thermodynamic data on the Ni–Si phases have been estimated from literature data in order to be in agreement with the experimental facts in the Ni–SiC system [7]. Besides, the $\Delta G^\circ$ value for Si$_3$N$_4$ at 1373 K differs between e.g. Barin and Knacke [9] ($-290$ kJ/mol) and Hendry [12] ($-318$ kJ/mol) which leads to the different plots in Fig. 5.

The results were surprising in the sense that for most pellet compositions the centre consisted of the

<table>
<thead>
<tr>
<th>Composition</th>
<th>Temperature (K)</th>
<th>$p_{N_2}$ (bar)</th>
<th>Vacuum</th>
<th>He + 18% H$_2$, 1 bar</th>
<th>$p_{N_2} = 2 \times 10^{-5}$ bar</th>
<th>$p_{N_2} = 0.8$ bar</th>
<th>$p_{N_2} = 100$ bar</th>
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</thead>
<tbody>
<tr>
<td>3Mo + Si$_3$N$_4$</td>
<td>1573</td>
<td>MoSi$_2$ + Mo$_3$Si$_3$</td>
<td>MoSi$_2$ + Mo$_3$Si$_3$</td>
<td>Mo$_3$Si$_3$ + Si$_3$N$_4$</td>
<td>Mo$_3$N + Si$_3$N$_4$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6Mo + Si$_3$N$_4$</td>
<td>1573</td>
<td>Mo$_3$Si$_3$ + Mo$_3$Si</td>
<td>Mo$_3$Si$_3$ + Mo$_3$Si</td>
<td>Mo$_3$N + Si$_3$N$_4$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20Mo + Si$_3$N$_4$</td>
<td>1573</td>
<td>Mo$_3$Si + Mo</td>
<td>Mo$_3$Si + Mo</td>
<td>Mo$_3$N + Si$_3$N$_4$</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Composition</th>
<th>Temperature (K)</th>
<th>$p_{N_2}$ (bar)</th>
<th>Vacuum</th>
<th>Ar + 10% H$_2$, 1 bar</th>
<th>$p_{N_2} = 2 \times 10^{-5}$ bar</th>
<th>$p_{N_2} = 0.5$ bar</th>
<th>$p_{N_2} = 1$ bar</th>
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</thead>
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<tr>
<td>3Ni + 2Si$_3$N$_4$</td>
<td>1373</td>
<td>Centre Ni$_2$Si + Si$_3$N$_4$</td>
<td>Centre Ni$_2$Si + Si$_3$N$_4$</td>
<td>Centre Ni$_2$Si + Si$_3$N$_4$</td>
<td>Centre Ni$_2$Si + Si$_3$N$_4$</td>
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<tr>
<td>3Ni + Si$_3$N$_4$</td>
<td>1373</td>
<td>Centre Ni$_2$Si + Si$_3$N$_4$</td>
<td>Centre Ni$_2$Si + Si$_3$N$_4$</td>
<td>Centre Ni$_2$Si + Si$_3$N$_4$</td>
<td>Centre Ni$_2$Si + Si$_3$N$_4$</td>
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<td>1373</td>
<td>Centre Ni$_3$Si + Si$_3$N$_4$</td>
<td>Centre Ni$_3$Si + Si$_3$N$_4$</td>
<td>Centre Ni$_3$Si + Si$_3$N$_4$</td>
<td>Centre Ni$_3$Si + Si$_3$N$_4$</td>
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Fig. 5. Solid phases in equilibrium with solid Si$_3$N$_4$ in the Ni–Si–N system as a function of temperature and nitrogen partial pressure according to thermodynamic data on nickel silicides based on Ref. [7]. In (a) the thermodynamic data for Si$_3$N$_4$ are taken from Ref. [9], in (b) from Ref. [12].
phases Ni$_3$Si + Si$_3$N$_4$. The outer gas atmosphere had little or no influence except for those experiments performed in a vacuum atmosphere where δ-Ni$_2$Si was found in the centre. All pellets showed a dense scale of Si$_3$N$_4$ with isolated particles of elemental nickel with some silicon dissolved in it; in vacuum we did not find such a scale.

These results are in contradiction with the expectations based on Fig. 5 and we can think of only one possibility. The dense outer scale, formed around the pellets blocks the release of nitrogen gas. If in the pellet a pressure of about 0.1 atm of nitrogen is created by this effect, the experimental results are consistent with the theoretical predictions (see Fig. 5).

The formation of the dense outer scale might arise from the influence of the atmosphere on the sintering process. The locally good contact interface between the Ni particles and Si$_3$N$_4$ in this scale makes it even more difficult for N$_2$ to escape than in the centre of the pellet, where use can be made of local cracks in the outer scale. This situation is comparable with that in diffusion couples using dense Si$_3$N$_4$. We will see in Section 3.2 that indeed the same reaction product is present in these couples at the interface with Si$_3$N$_4$, viz. the solid solution of Si in Ni.

3.2. Diffusion couples

3.2.1. Mo–Si$_3$N$_4$. In all diffusion couples consisting of Mo and dense Si$_3$N$_4$ only one phase was formed at the interface, viz. Mo$_2$Si, independent of the external nitrogen partial pressure. This layer is very irregular and many cracks can be observed, see Fig. 6. The morphology of the reaction layer does not depend on the type of additives in the dense Si$_3$N$_4$, although a layer of 2MgO·SiO$_2$ develops by segregation at the interface between Si$_3$N$_4$ and Mo$_2$Si in couples with MgO-doped Si$_3$N$_4$.

However, at the triple point of the couple where both starting materials are in contact with the gas atmosphere other phenomena occur, as shown schematically in Fig. 7. At N$_2$ partial pressures of $6 \times 10^{-10}$ and $2 \times 10^{-5}$ bar, layers of MoSi$_2$, Mo$_5$Si$_3$, and Mo$_3$Si were formed on the Mo parts which protruded from the couple.

At a N$_2$ partial pressure of 0.8 bar, only Mo$_3$Si and Mo$_5$Si$_3$ were formed. This is in complete accordance with the expectations from Figs 3 and 4, which predict MoSi$_2$ and Mo$_5$Si$_3$, respectively, in equilibrium with Si$_3$N$_4$. The more Mo-rich silicides are then formed through the reaction between the parent Mo material and these phases. These triple point phenomena do not occur at an annealing temperature of 1373 K.

3.2.2. Ni–Si$_3$N$_4$. In this system, measurements are still in progress at 1373 K. In all experiments up to 120 h annealing time, we did not find any intermetallic compound at the interface when dense Si$_3$N$_4$ was used. The maximum solid solubility of about 15 at. % Si in Ni was found at the metal side of the interface. The penetration curve of Si into Ni reached as far as 400 μm into the nickel substrate. A cross
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Fig. 9. Diffusion couple between Mo and 50\% porous Si₃N₄, annealed 50 h at 1573 K in vacuum. The original Mo-foil has been converted completely into the phases Mo₅Si₃ (middle part) and MoSi₂ (in equilibrium with Si₃N₄). The length of the white bar is 10 μm.

section of this couple is shown in Fig. 8 and is representative for all couples with dense Si₃N₄, independent of the gas atmosphere.

The porous zone near the interface represents the position of the original Si₃N₄ material that has been converted into a metal solid solution. This, in fact, indicates the position of the Kirkendall plane and shows that at 1373 K both Ni and Si take part in the diffusion process. Up to 150 μm from the interface, very small precipitates of Ni₃Si are formed in the nickel phase which developed during cooling, which for this particular couple was about 50°C per h.

Like the case of Mo-Si₃N₄ couple annealed at 1373 K, no other reaction products could be found at the triple point of these couples. Probably the presence of oxygen plays an important role as will be discussed in section 3.3.

3.2.3. Discussion of the diffusion couples. When we look to Fig. 3(c), and try to predict the type and sequence of the reaction products in a Mo-Si₃N₄ diffusion couple at one atmosphere partial pressure of N₂, we would suggest the sequence Mo-Mo₃Si-Mo₅Si₃-(N₂)-Si₃N₄ according to the reasoning given earlier for diagrams of the type shown in Fig. 2. However, we only find Mo₃Si as a product at the interface, independent of the partial N₂ pressure. These results suggest that the gas atmosphere surrounding the couple does not influence the interface reaction in the centre of the couple. This becomes quite clear from considering that N₂ gas has to escape somehow from the interface in the interior and this is difficult in fully dense diffusion couples. Therefore, a nitrogen pressure will build up at this interface. According to our calculations for the Mo-Si₃N₄ system, this pressure is between 7 and 88 bar, because Mo₅Si has been found in equilibrium with Si₃N₄ but Mo₂N has not been formed. For Ni-Si₃N₄ this

![Stability diagram](image)

Fig. 10. A stability diagram of the solid phases in the Si–N–O system at 1573 K as a function of the partial pressures of oxygen and nitrogen according to the data of Refs [9] and [12]. The dashed line shows the locus of constant SiO₂-partial pressures of 10⁻⁶ bar. The dotted lines separate the stability region of the various Mo-silicides based on Fig. 4.
pressure must be >27 bar [Fig. 5(b)] or >91 bar [Fig. 5(a)]. (In fact, one should speak about the fugacity of N₂ instead of its partial pressure.) This is corroborated by the diffusion couple experiments between Mo and 50% porous Si₃N₄. As seen in Fig. 9, very thick layers consisting of MoSi₂ and Mo₃Si are formed between Si₃N₄ and Mo. 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 N₂ can escape through the open pores in the Si₃N₄. Therefore, the reaction layer sequence corresponds with the thermodynamic calculations. In the next section we will discuss the influence of oxygen on this process. It will turn out that the formation of SiO gas, possible in some of our experimental conditions, is responsible for the formation of Mo-silicides on the protruding Mo-parts in the diffusion couple.

3.3. The influence of oxygen

Using the thermodynamic data given by Hendry [12] and Barin and Knacke [9] it is possible to draw a phase stability diagram for the solid Si-O-N phases at 1573 and 1373 K as shown in Figs 10 and 11. These figures show that under whatever conditions of vacuum or inert gas, the phase SiO₂ is always present as an outer layer on Si₃N₄ if thermodynamic equilibrium is established. Both phases are then separated by the oxynitride Si₂ON₂. In reducing atmospheres these oxide films can be removed, especially at higher temperatures as is seen from a comparison between Figs 10 and 11. In these figures the H₂O/H₂ ratio and the SiO pressure is shown corresponding with the oxygen and nitrogen partial pressures. The dashed line in Fig. 10, for instance, shows the locus of all O₂ and N₂ pressures at which pSiO = 10⁻⁶ bar. The review article of Heuer and Lou [11] is an excellent guide for reading this type of diagram.

It can be seen from this figure that the SiO-pressure reaches a maximum value at the Si-SiO₂ interface. Under the circumstances mentioned in Fig. 7, the SiO-pressure is large enough to form silicides at the surface of the protruding Mo foil in the Mo-Si₃N₄ couple at 1573 K. This was shown by the fact that the same silicides were formed at the surface of Mo slices which were not in direct contact with Si₃N₄ but separated from Si₃N₄ at a distance of about 0.1 mm. The reaction equation Mo + 2SiO₉(gas) → MoSi₂ + O₂ is
thermodynamically more favourable under the experimental conditions than the triple point reaction if only Mo and Si₃N₄ are considered without oxygen, which is the sum of the reactions Si₃N₄→3Si(α) + 2N₂ and 1.5 Mo + 3Si(α)→1.5 MoSi₂. At 1373 K the SiO pressure is too low to provide enough Si transport, and therefore silicides are not formed on molybdenum or nickel at 1373 K, as was shown experimentally.

More important even are the dotted lines shown in Figs 10 and 11. These show the oxygen and nitrogen pressures at which two solid phases from the Mo-Si or Ni-Si system are in equilibrium with either Si₃N₄, Si₂ON₂ or SiO₂. The lines can be found by drawing the constant Si activity line belonging to the equilibrium between these two solid phases. The course of the dotted lines in the Si₃N₄ phase field, for instance, agree with the N₂-pressure shown in Figs 4 and 5(b). If the oxygen partial pressure becomes so high that Si₂ON₂ or SiO₂ become stable, the N₂ partial pressure at which these phases can coexist obviously becomes lower. Therefore, the presence of thin films of e.g. oxynitride on Si₃N₄ might influence the pressure build-up of nitrogen at the interface with Mo or Ni. Currently, experiments are going on in both systems to verify the predictions made on thermodynamic grounds on metal-ceramic interactions in mixed O₂/N₂ atmospheres.

4. CONCLUSIONS

The main conclusions from our work so far are:

—The reaction products in dense diffusion couples between metals and Si₃N₄ are independent of the surrounding gas atmosphere.

—The experimental results can be explained by assuming a N₂-pressure build-up at the interface. This is relevant for the joining technology of Si₃N₄ with metals which do not form nitrides.

—The oxygen partial pressure in the gas atmosphere might play an important role. This is established from the triple point-effects, caused by SiO gas formation.

—Sintering additives do not play a decisive role, although the frequently occurring MgO-dopant in Si₃N₄ segregate to the interface, forming a layer with 2MgO·SiO₂ particles.

The experimental results on equilibrated powder mixtures annealed under a controlled gas atmosphere can help the assessment of correct thermodynamic data. Using these data, phase stability plots can be constructed which have predictive value for the phenomena found in sintering experiments (or in diffusion couples in which porous Si₃N₄ is used). Comparing these plots with the actual composition at the metal–Si₃N₄ interface in dense diffusion couples leads to an estimate of the built-up nitrogen pressure at this interface. However, the formation of densely sintered outer scales on the pellets introduces different partial N₂pressures inside the pellet which must be taken into account.

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