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Stability and formation kinetics of TiN and silicides in the Ti/Si_3N_4 diffusion couple

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ABSTRACT

Reactions in Ti/Si_3N_4 and TiN/Si diffusion couples annealed in the temperature range of 1000-1200°C were studied theoretically as well as experimentally with SEM/EPMA technique. Isothermal sections of the Ti-Si-N system were calculated using the most recent thermodynamic data. Calculations showed that TiN and Si react with each other and form Si_3N_4 and $TiSi_2$, parallel to the experimental studies. Correspondingly, results from the Ti/Si_3N_4 couple were in good accordance with calculated phase equilibria.

INTRODUCTION

Silicon nitride is one of the most promising materials among technical ceramics, used in structural components for high temperature applications as well as in electronics industry. Brazing with active filler metals is the preferred method of joining Si_3N_4 to other ceramics and metals. When titanium is present with high activity, it is able to dissociate chemically most stable compounds, and therefore a few percentages of Ti is commonly added into the filler alloys. Since chemical reactions between Ti and Si_3N_4 are decisive, e.g. in active brazing, the Ti-Si-N system is one of the most important parts of the brazing system. Thus, a consistent thermodynamic description of the Ti-Si-N system is needed. This description is important also for the studies on the growth kinetics of the reaction products.

Beyers et al. (1) and Schuster et al. (2) have published calculated ternary isotherms of the Ti-Si-N system. In these papers Ti_5Si_3 is presented as a line compound and all silicides are in equilibrium with TiN_x. The notable difference between the diagrams is the equilibrium between TiN_x and Si, which is present in Beyers´s diagram but not in the Schuster´s one. Wakelkamp (3) has studied the system also experimentally and observed the solubility of nitrogen in Ti_5Si_3 to be about 11 at-%. There is the equilibrium between TiN_x and Si in Wakelkamp´s diagram, which was determined on the basis of the diffusion couple experiments.

To investigate the system in more detail and to clarify the mentioned omissions and inconsistencies, Ti/Si_3N_4 and TiN/Si diffusion couple experiments were carried out in a high vacuum furnace. The diffusion couples were examined with the SEM/EPMA technique. Since more recent thermodynamic data are now available, the ternary isothermal section of the Ti-Si-N system was assessed using the Thermo-Calc databank system (4).

MULTIPHASE DIFFUSION

The formation of a phase sequence in a binary diffusion couple can be predicted directly from the relevant phase diagrams. After long annealing all the thermodynamically stable phases will exist as single

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phase regions between the end members - in accordance with the phase rule. Thicknesses of the layers are determined either by linear or parabolic growth kinetics. However, the metal-ceramic systems contain more than two elements, which makes the prediction of the reaction layers much more difficult.

In ternary diffusion couples also two-phase regions can form and therefore many phase sequences are possible. Naturally, diffusion paths in a ternary phase diagram must fulfill the conservation of mass. Since no material can be lost or created the diffusion path is forced to cross the straight line between the end members at least once. Using the model developed by van Loo (5) the actual phase sequence can often be predicted. The central idea in this model is that an element intrinsically diffuses only in the direction of its own decreasing activity.

THERMODYNAMIC DATA AND MODELS

The Ti-Si-N system was assessed using available thermodynamic data and the Thermo-Calc databank system. The Ti-Si system used in this study was taken from Pajunen et al. (6), which was optimized by using the known lattice stabilities for Ti and Si. The calculated Ti-Si phase diagram is consistent with the results of experimental measurements and optimized parameters have acceptable values as compared with the experimental Gibbs energies of the silicides. The data on TiN_x were taken from Ohtani and Hillert (7). The Gibbs energy of the formation of Si_3N_4 is given by Hillert et al. (8). The interstitial α-Ti and β-Ti solutions and the nonstoichiometric fcc-TiN_x were described with the two sublattice model, while the Ti_5Si_3[N] solution was modelled with three sublattices (6).

EXPERIMENTAL PROCEDURE

Two different diffusion couples were prepared: Ti/Si_3N_4 and TiN/Si. The high purity (99.99+) titanium and hot-pressed silicon nitride (95% Si_3N_4, rest Al_2O_3, Y_2O_3) specimens were cut from a rod of base material in thickness of about 2.0 mm. After grinding the Si_3N_4 samples were mechanically polished. The titanium samples were polished electrolytically at -35°C and etched subsequently in a 10%HF solution. The silicon specimens were cut from (100) single crystal wafers. The titanium nitride films were deposited by reactive ion plating (PVD) on the Si substrates in Ar:N_2 atmosphere. Before the evaporation of titanium the Si-substrates were sputter-cleaned. Microscopical examinations showed that no reaction layer formed during evaporation between the golden-coloured TiN-layer and silicon.

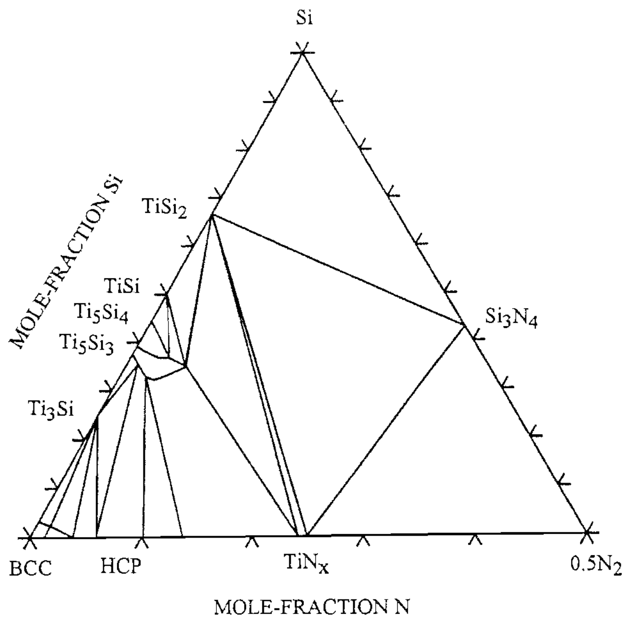
The Ti/Si_3N_4 diffusion couples were annealed in a vacuum furnace ($p<10^{-5}$mbar) at 1100°C for different periods of time. The pressure on the couple's interface was about 350 N/cm^2. The TiN/Si couples were annealed both in a vacuum furnace as well as in vacuum ampoulles at temperatures between 1000-1200°C up to 80 hour. The samples were examined with a scanning electron microscope equipped with WDS-units.

RESULTS AND DISCUSSION

Figure 1 shows the isothermal section of the Ti-Si-N system and the activity diagram for nitrogen both calculated at 1100°C. The isotherm is in close agreement with the one determined experimentally by Wakelkamp (3). Due to the solubility of nitrogen Ti_5Si_3 becomes in equilibrium with all other silicides. Contrary to Wakelkamp's results the calculated diagram shows an equilibrium between Si_3N_4 and $TiSi_2$ instead of the Si-TiN equilibrium.

Ti/Si3N4 Diffusion joint

Figure 2a) shows the SEM micrograph from the interface of the Ti/Si_3N_4 diffusion couple after annealing at 1100°C. The joints were invariably fractured along the interface next to the Si_3N_4. The formation of TiN_x, adjacent to the Si_3N_4, in the Ti/Si_3N_4 couple is suggested earlier in similar studies (3,9). The TiN_x could not be detected in this study and it is likely that the joint has fractured between the TiN_x layer and the layer consisting of Ti_5Si_3[N] and α-Ti[N,Si] solid solution (I in Fig 2a). The qualitative analysis revealed nitrogen in both of these phases. From integral measurements of nitrogen in



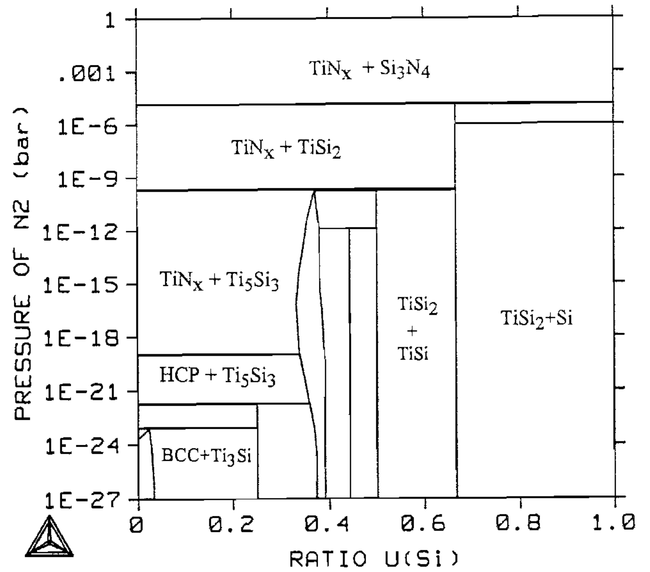
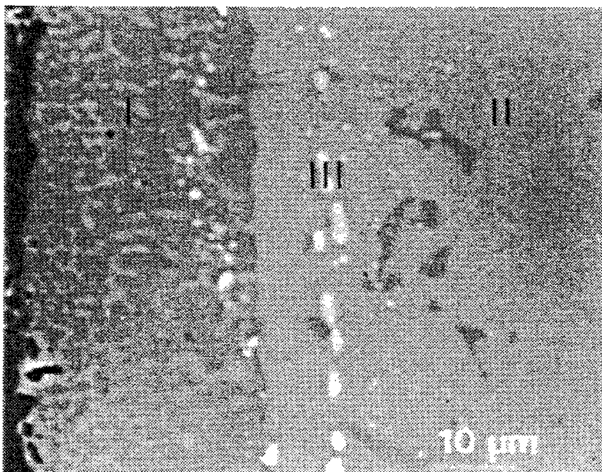


Figure 1 a) Phase diagram of the Ti-Si-N system at 1373K

b) Activity of nitrogen (N_2) as a function of the u_{Si} ($= x_{Si}/(x_{Si} + x_{Ti})$.

Ti_5Si_3 with EPMA the solubility of nitrogen in this phase was found to be about 11 at.% (3). After 40 hours´ annealing the reaction layer (Ti_5Si_3[N]+α-Ti[N,Si]) is abt. 29 μm thick. The overall reaction layer extends up to 500 μm with a wide layer consisting of the α-Ti solution and particles of the Ti_5Si_3[N] (II in Fig 2a), which are precipitated during cooling. There are also two rows of light coloured Y_2O_3 particles (III in Fig 2a). On the basis of the above results the layer sequence is: Si_3N_4/TiN_x/Ti_5Si_3[N]+α-Ti(prec.)/α-Ti/β-Ti. The diffusion path is shown in figure 2b.



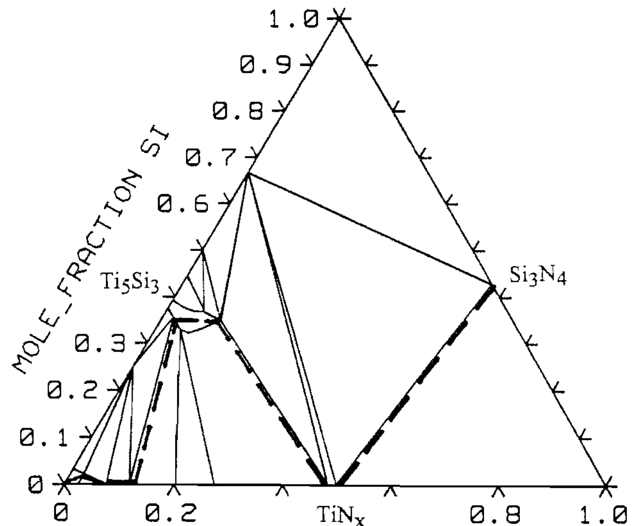


Figure 2 a) SEM-micrograph of the Ti/Si_3N_4 diffusion couple annealed at 1100° for 40 hours

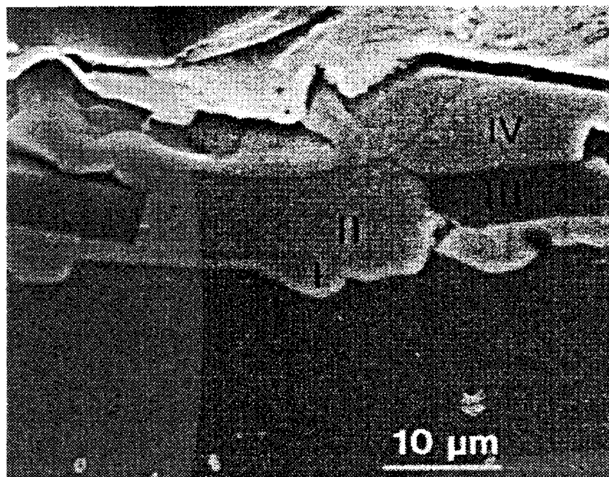
b) diffusion path between Ti and Si_3N_4 at 1100°C

TiN/Si Diffusion joint

After 70 hours´ annealing of the TiN/Si couple in vacuum ampoulles at 1100°C a thin layer of $TiSi_2$ was formed between TiN and Si, about 1/10 of the thickness of the applied TiN coating of about 6 μm. It is likely, that the nitrogen released in the reaction dissolves in the TiN solid solution, which might not be fully saturated with N.

Also in another experiment, made in the vacuum furnace at 1050°C for 80 hours, the $TiSi_2$ layer was found next to the silicon (I in Fig 3a). The TiN_x layer (II in Fig 3a), originally about 4 µm thick, has largely transformed to Si_3N_4 (III in Fig 3a). On the top of the specimen there is a thin layer of $TiSi_2$ (IV in Fig 3a), which is most likely formed in the reaction between TiN and Si in the gas phase. This experiment shows, that under the experimental conditions we worked the phase equilibrium exists between $TiSi_2$ and Si_3N_4 (Fig 3b).

The difference with the results of other investigatiors is presumably caused by impurities, especially oxygen. In principle, it is possible that dissolved oxygen stabilizes TiN_x and thereby prevents its reaction with silicon. On the other hand, the reaction may be impeded by the presence of a thin SiO_2 layer on the silicon, if this is not carefully removed during the experiments. Further experiments are carried out at the moment in order to investigate in more detail the influence of the experimental conditions on the phase relations and the reactions in the Ti-Si-N system.



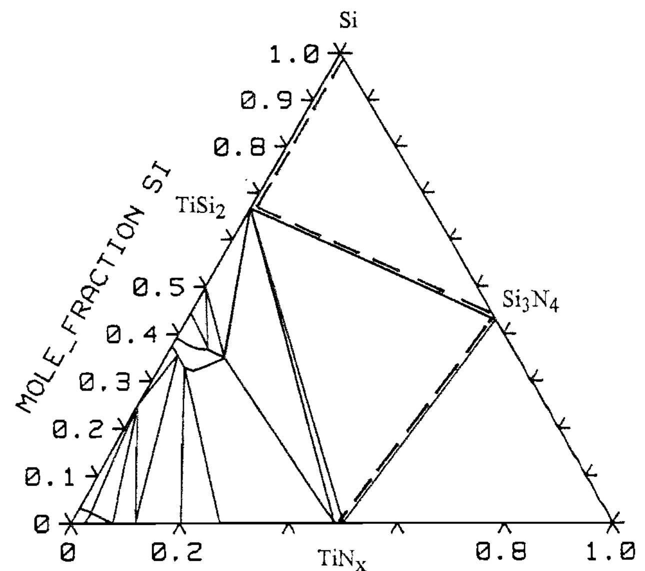


Figure 3 a) SEM-micrograph of the TiN/Si diffusion couple annealed at 1050° for 80 hours

b) diffusion path between TiN and Si at 1050°C

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