Solid state reactions in the Ag-Ti-Si system: periodic layer formation
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The isothermal cross-section through the ternary phase diagram Ag–Ti–Si at 1123 K was determined by means of multiphase diffusion couples. No ternary phases are present on this Ag–Ti–Si isotherm. A thermodynamic assessment of this system was performed using the data from the binary systems.

The formation of a periodic structure consisting of alternating layers of titanium-silicides and silver was observed in “sandwich” diffusion couples Ag/Ti-foil/Si after annealing between 1023 K and 1123 K. It was attributed to the internal reaction between titanium and silicon within the Ag-layer formed in situ during the solid state interaction. This process, periodic in space and time, resembles the well-known Liesegang phenomenon.

1 Introduction

The present study was initially aimed at the experimental determination of the isothermal cross-section of the ternary Ag–Ti–Si phase diagram at 1123 K. The practical interest for this system is generated by the fact that Ag–Ti binary alloys are used as a base in commercial filler metals for brazing various Si-containing ceramics (e.g. SiC, Si3N4). Knowledge of this system is needed in order to predict the reaction products which can be formed within the brazing seam during fabrication or during high-temperature exposure of the joints.

Using both the semi-infinite diffusion couple technique (mainly with multiphase alloys as end-members) and finite “sandwich” diffusion couples like Ag/Ti-foil/Si the isothermal cross-section through the ternary Ag–Ti–Si diagram at 1123 K was constructed. Using the finite sandwich couple technique a peculiar periodic layer formation was found which gave rise to an additional investigation parallel to the initial phase diagram study.

2 Experimental Details

Silver (99.99% purity) and titanium (99.98%) supplied by Goodfellow (UK) and silicon (99.98%) (Hoboken, Belgium) were used as initial materials. Alloy ingots of nominal composition Ti60Ag20, Ti60Ag40, Ti73Si25 were prepared by arc-melting under argon. The specimens were annealed in evacuated silica capsules at 1123 K for 120 h and quenched in water. The temperature was controlled within ±3 K.

From the annealed ingots slices of approximate dimensions 5 x 5 x 1.5 mm³ were cut and their bonding faces were ground and polished to a final finish with 0.25 μm alumina slurry.

Before bonding, all samples were ultrasonically cleaned in ethanol and then dried using a hot air blower. The diffusion couples were heat-treated in a vacuum furnace (5 x 10⁻⁶ mbar) under an external load of 2 MPa. Temperature control was performed within ±2 K accuracy. The actual temperature at the place of the sample might deviate ±5 K from the values reported in this paper.

After annealing and standard metallographic preparation the diffusion couples have been examined by polarized light microscopy, scanning electron microscopy (SEM) and electron probe microanalysis (EPMA).

3 Results and Discussion

3.1 Phase Equilibria in the Ag–Ti–Si System at 1123 K

3.1.1 Reactions Between Two-phase Ti–Ag Alloys and Si at 1123 K

The microstructure of the transition zone between silicon and a two-phase (α-Ti + Ti2Ag) alloy with the nominal composition Ti60Ag20 after annealing at 1123 K for 120 h is given in Fig. 1. Continuous layers of the intermetallic compounds TiSi2 and TiSi were found at the Si-side of the diffusion couple, and continuous layers of the binary intermetallics TiAg and Ti5Ag were observed next to the initial two-phase alloy. The TiAg layer is separated from the titanium silicides by a thin layer of pure silver (Fig. 1b). No silver was detected in TiSi2 and TiSi and likewise no appreciable solubility of Si in TiAg was found.

When a two-phase alloy Ti60Ag40 consisting of Ti2Ag and TiAg as used as end-member the reaction with silicon at 1123 K for 120 h led to the formation of three layers of titanium silicides: TiSi2, TiSi and Ti5Si3 (Fig. 2). Next to the initial two-phase alloy a continuous layer of TiAg was formed. Again this layer is separated from the titanium silicides by a layer of silver (Fig. 2b). The solubility of silver in the silicide phases as well as that of silicon in the intermetallic compound TiAg is below the detection limit of EPMA.

The formation of a continuous layer of Ag between Ti5Si3 and TiAg is a strong indication that at this temperature the titanium silicides TiSi2, TiSi and Ti5Si3 cannot be in equilibrium with TiAg.
In both couples the position of the Kirkendall plane nearly coincides with the Si/TiSi interface, showing that the total reaction layer is formed by diffusion of Si into the original two-phase alloys.

3.1.2 The Interaction Between Silver and a Non-equlibribated Ti75Si25 Alloy at 1123 K

In Fig. 3 the microstructure of the reaction zone in the diffusion couple Ti75Si25/Ag after annealing at 1123 K for 144 h is given. A rim of Ti5Si3 around the Ti5Si1 particles in the initial alloy underlines the peritectoid reaction β-Ti + Ti5Si3 ⇌ Ti5Si in the binary TiSi system as shown in Fig. 4 [1]. The morphology of the alloy can therefore be attributed to a non-equilibrium situation. Obviously, the heat-treatment of the Ti75Si25 alloy for 120 h at 1123 K was not sufficient to equilibrate the alloy. For a phase diagram investigation this is not necessarily a disadvantage. For instance, it can be seen from Fig. 3 that the particles of Ti5Si1 originally present in the starting binary alloy still

Figs. 1a and b. Reaction zone of a Si/(α-Ti + Ti5Ag)-alloy diffusion couple, annealed for 120 h at 1123 K in vacuum (Backscattered Electron Images (BEI)); (a) general view; (b) magnified area showing the thin continuous silver layer.

Figs. 2a and b. Reaction zone of a Si/(Ti2Ag + TiAg)-alloy diffusion couple (BEI), annealed for 120 h at 1123 K in vacuum; (a) general view; (b) magnified area showing the thin continuous silver layer.

Figs. 3a and b. Reaction zone of a Ag/Ti75Si25-alloy (nominal composition) diffusion couple (BEI) annealed for 144 h at 1123 K in vacuum; (a) (left) general view; (b) (right) magnified interfacial region.
can coexist inside the reaction zone with silver and TiAg, but not with Ti2Ag. On the other hand, Ti3Si coexists with both intermetallics TiAg and Ti2Ag and with α-Ti. This proves the presence of the three-phase equilibria Ti5Si3 + TiAg + Ag, Ti5Si3 + Ti3Si + TiAg, Ti3Si + TiAg + Ti2Ag and Ti3Si + Ti2Ag + α-Ti in the Ag–Ti–Si system at 1123 K.

No evidence was found for the presence of ternary phases, and all equilibria found in the described experiments are consistent with the ternary Ag–Ti–Si isotherm shown in Fig. 5. Theoretically it is possible that ternary phases exist in this system which did not nucleate in our samples, but in view of the consistency of the proposed isotherm with the finite sandwich experiments described in Section 3.2 this is very improbable. The same phase relations are obtained from a thermodynamic assessment of the Ag–Ti–Si system as is shown in Section 3.1.3.

3.1.3 Thermodynamic Aspects of the Ag–Ti–Si System

Values for the standard Gibbs energy of formation of the intermetallic compounds in the Ti–Si system at 1123 K as given in Table 1 were derived from [2], except the one for Ti3Si as will be explained later. The data on the Ti–Ag system are the same as used in our previous work on the Ag–Fe–Ti system [3]. All intermetallic phases were treated as line compounds.

When using the value $\Delta G^{\ominus}(\text{TiSi}) = -214.5$ kJ/mol as derived from Ref. [2] the phases Ti3Si and Ag should be in equilibrium which conflicts with our experimental results. If we do not want to change the data for the other phases and we want to get a negative standard Gibbs energy for the reactions $3 \text{Ti}_2\text{Si} + 4 \text{Ag} \rightarrow \text{Ti}_5\text{Si}_3 + 4 \text{TiAg}$ and $\text{Ti}_3\text{Si} + 4 \text{Ti}_2\text{Ag} \rightarrow 3 \text{Ti}_2\text{Si} + 4 \text{TiAg}$, as required by the experimentally determined isotherm, we need to have $-198.5 < \Delta G^{\ominus}(\text{TiSi}) < -195.1$ kJ/mol. The value of $-197.0$ kJ/mol appearing in Table 1 is the value chosen by us. This is not an unrealistic procedure in view of the large influence of impurities on the stability of TiSi with respect to α-Ti and Ti3Si [4]. With this adjustment the experimental results on the Ag–Ti–Si system are in agreement with the thermodynamic predictions. The calculated activities of the elements in the three-phase fields are presented in Table 2.

3.2 The Formation of Periodic Structures in the Couples Ag/Ti-foil/Si

3.2.1 On Solid State Diffusion in the Ag–Ti–Si System

Binary diffusion couples Ti/Si and TiAg and sandwich samples TiAg(foil)/Si were used to obtain information on the diffusion kinetics and the growth of intermetallic

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta G^{\ominus}$ [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiSi2</td>
<td>-163.4</td>
</tr>
<tr>
<td>TiSi</td>
<td>-136.1</td>
</tr>
<tr>
<td>Ti5Si3</td>
<td>-647.0</td>
</tr>
<tr>
<td>Ti3Si</td>
<td>-582.1</td>
</tr>
<tr>
<td>TiSi</td>
<td>-197.0</td>
</tr>
<tr>
<td>Ti2Ag</td>
<td>-4.2</td>
</tr>
<tr>
<td>TiAg</td>
<td>-3.4</td>
</tr>
</tbody>
</table>

Table 1. Standard Gibbs energy of formation for the compounds of the Ag–Ti–Si system at 1123 K.

Table 2. The chemical activities of the elements in the three-phase fields of the Ag–Ti–Si system at 1123 K.

<table>
<thead>
<tr>
<th>Area2</th>
<th>Activity1</th>
<th>Activity1</th>
<th>Activity1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$a_{\text{Si}}$</td>
<td>$a_{\text{Ti}}$</td>
<td>$a_{\text{Ag}}$</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>2.1 $\cdot$ 10^{-8}</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>0.05</td>
<td>9.3 $\cdot$ 10^{-6}</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>0.027</td>
<td>1.74 $\cdot$ 10^{-5}</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>9.7 $\cdot$ 10^{-4}</td>
<td>2.47 $\cdot$ 10^{-4}</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>1.6 $\cdot$ 10^{-9}</td>
<td>0.72</td>
<td>0.963</td>
</tr>
<tr>
<td>6</td>
<td>1.4 $\cdot$ 10^{-9}</td>
<td>0.79</td>
<td>0.94</td>
</tr>
<tr>
<td>7</td>
<td>8.9 $\cdot$ 10^{-10}</td>
<td>0.92</td>
<td>0.76</td>
</tr>
<tr>
<td>8</td>
<td>7.8 $\cdot$ 10^{-10}</td>
<td>0.963</td>
<td>0.69</td>
</tr>
</tbody>
</table>

1) Activities calculated using the stable pure elements as the reference state.
2) Corresponding numbers are depicted in Fig. 5.
3) Calculated assuming Raoult's behaviour.
compounds in the Ag-Ti-Si system at 1123 K. In Fig. 6 the microstructure of the reaction zone in a binary diffusion couple Ti/Si after annealing in vacuum for 415 h at 1123 K is shown. TiSiz and TiSi are the predominant layers. Ti-rich silicides (Ti3Si, Ti5Si3, and Ti5Si) were found to grow much slower. The Kirkendall plane is revealed by the row of pores located close to the Si/TiSiz interface. These pores result from the removal (during polishing) of small HfO2 particles (0.25 to 0.5 μm) which had been placed as inert markers on the surface of Ti prior to joining. The position of the Kirkendall plane shows that silicon is the main diffusing species in the TiSiz phase.

Reaction of Ti in the diffusion couple with Ag at 1123 K leads to the formation of two continuous layers TiAg and Ti2Ag (Fig. 7). The Kirkendall plane is visible as a row of pores that coincides with the Ag/TiAg interface, proving that silver is by far the most mobile species in TiAg.

The thicknesses of the phases formed in the diffusion couple are directly related to the interdiffusion coefficients in these phases. However, when an intermetallic compound with a very narrow region of homogeneity grows during the reaction diffusion (like in the binary couples Ti/Si and Ti/Ag) it is impossible to measure a concentration gradient in these phases and therefore the conventional Matano-Boltzmann analysis for evaluating interdiffusion coefficients cannot be applied. To avoid this problem, the integrated diffusion coefficient was introduced by Wagner [5]. This coefficient, a materials constant, is defined as the interdiffusion coefficient of a phase integrated over its (unknown) limits of homogeneity. More details about the use of this concept can be found elsewhere [6]. In Table 3 values of the average integrated diffusion coefficients in different intermetallic compounds of the Ag-Ti-Si system at 1123 K are listed. They are calculated using average layer widths in all couples; differences in molar volumes of the phases were taken into account. Knowledge of the values of the integrated diffusion coefficients makes it possible to calculate the thicknesses of the layers formed in a binary diffusion couple no matter which starting materials are used. The same is true in a ternary system in the absence of ternary phases or ternary solid solutions as is the case for the present Ag-Ti-Si system, but then the activities of the elements at the phase interfaces should be known [6] as are given in Table 2.

When 100 μm foil of silver was pressed between slices of silicon and titanium (of a few mm thickness) and annealed in vacuum at 1123 K for 64 h, the formation of Ti-silicides was found close to the TiAg/Ag interface (Fig. 8). This indicates that silicon diffuses much faster than titanium through solid silver.

### 3.2.2 Morphological Evolution of the Diffusion Zone in Ag/Ti-foil/Si Diffusion Couples

When a "sandwich" sample Ag/Ti-foil/Si was heat-treated for a sufficiently long time (depending on the thickness of the Ti-foil) the formation of a periodic structure in the reaction zone was observed (Fig. 9).

The microstructure consists of a continuous layer of TiSiz; adjacent to the silicon and a layer of TiAg next to the initial Ag end-member. The two-phase zone between those layers consists of more or less regular alternating layers of Ti-silicides and pure silver parallel to the original interface. The morphology of the silver bands within this structure is an

<table>
<thead>
<tr>
<th>Phase</th>
<th>( V_m ) [10^{-5} m^3/mole of atoms]</th>
<th>( D_{int} ) [10^{-18} m^2/s]</th>
<th>Phase</th>
<th>( V_m ) [10^{-5} m^3/mole of atoms]</th>
<th>( D_{int} ) [10^{-18} m^2/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti3Si</td>
<td>1.00</td>
<td>4 ± 2</td>
<td>Ti2Ag</td>
<td>1.04</td>
<td>70 ± 30</td>
</tr>
<tr>
<td>Ti5Si3</td>
<td>0.92</td>
<td>5 ± 2</td>
<td>TiAg1</td>
<td>1.03</td>
<td>1830 ± 200</td>
</tr>
<tr>
<td>Ti5Si</td>
<td>0.91</td>
<td>11 ± 3</td>
<td>Ag</td>
<td>1.03</td>
<td>-</td>
</tr>
<tr>
<td>TiSi</td>
<td>0.90</td>
<td>120 ± 50</td>
<td>Si</td>
<td>1.21</td>
<td>-</td>
</tr>
<tr>
<td>TiSiz</td>
<td>0.85</td>
<td>890 ± 50</td>
<td>Ti</td>
<td>1.06</td>
<td>-</td>
</tr>
</tbody>
</table>

1 Ti5Si and TiAg have been treated as line compounds.
intermittent layer arrangement while the Ti-silicide layers exhibit a continuous interconnected and slightly tortuous pattern. A continuous layer of silver was found next to TiAg. This layer always separates TiAg from the titanium silicides.

The silicides present inside the periodic structure are Ti$_2$Si$_2$ (close to the continuous layer of Ti$_2$Si$_2$), TiSi and, for a number of samples, Ti$_5$Si$_4$, depending on the initial thickness of the Ti-foil and on the annealing time at a specified temperature. Whether or not a TiAg layer is present in the diffusion zone depends on the thickness of the Ti-foil used and the annealing time, because the TiAg layer is consumed in the course of the reaction. The microstructure shown in Fig. 9d might be considered as the final stage of such a morphological evolution. The titanium initially present in the diffusion zone has been completely converted into Ti$_2$Si$_2$.

In the binary Ag–Si system a eutectic melting point is found at 1118 K and 11 at.% Si [11]. No indication of liquid phase formation was found in the sandwich couples annealed at 1123 ± 5 K, in accordance with the fact that no Si was detected in the silver bands formed in the reaction zone. However, in order to be sure that no liquid phase might be involved in the periodic pattern formation, a number of similar experiments were performed at 1023 K and 1073 K, far below the eutectic isotherm in the Ag–Si system. They all showed the same reaction layer morphology.

3.2.3 Proposed Reaction Mechanism Leading to Periodic Pattern Formation

The series of events with increasing annealing time for a sandwich couple Ag/Ti-foil/Si is schematically depicted in Fig. 10. As long as pure α-Ti is present in the transition zone between the Ti-silicides and Ti$_2$Ag, the growth of intermetallic phases is governed by the diffusion kinetics of the respective binary systems Ti–Si and Ti–Ag (Fig. 10a). As soon as the Ti foil is completely converted into intermetallic compounds, the binary TiSi and TiAg couples constituting the sandwich couple are not semi-infinite anymore. In fact, Ti$_3$Si and Ti$_2$Ag will meet (Fig. 10b). According to the phase diagram (Fig. 5) these phases can exist in equilibrium, but the reaction will proceed because of the Si and Ag activity gradients which are still present in the diffusion couple. Silver diffuses through the TiAg layer and reacts with Ti$_2$Ag until the entire layer of Ti$_2$Ag is converted into TiAg (Fig. 10c). The same holds for the TiSi couple: Si atoms are still moving through the reaction product layers. Ti$_3$Si will transform into Ti$_5$Si$_4$ and onwards into Ti$_5$Si$_2$. This process will eventually bring the Ti$_5$Si$_2$ layer into contact with the TiAg layer. Since those layers cannot be in equilibrium, Si-atoms diffusing through the product layer will react at the TiAg/Ti$_5$Si$_2$ interface according to the reaction: 5 TiAg + 4 [Si] → Ti$_5$Si$_2$ + 5 Ag. As a result a continuous layer of silver will form at the TiAg side, separating the TiAg and Ti$_5$Si$_2$ layers (Fig. 10d).

These phase sequences were experimentally observed in the transition zone of the sandwich sample Ag/Ti-foil(50 µm)/Si after annealing in vacuum at 1073 K for 100 h (Fig. 11). In the part of the diffusion zone designated...
A (Fig. 11a) α-Ti is not completely exhausted, in region B (enlarged in Fig. 11b) the Ti-foil was consumed and TiAg is indeed separated from Ti₅Si₄ by a thin band of Ag. The point is now to explain the observed periodic structure, i.e. the transition from the morphology in Fig. 11b to that shown in Fig. 11c (region C in Fig. 11a).

A number of mechanisms has been put forward to explain the formation of resembling periodic layered structures found in different solid state systems like Fe₃Si/Zn, Co₃Si/Zn and SiC/Ni, either based on a periodic build-up and relaxation of stresses [7], on a periodic instability of the substrate/reaction product interface [8] or nucleation of bands through composition fluctuations [9]. Periodic layered zones of precipitates have also been observed in internal oxidation [10, 11] and internal reduction [12] of solids and were explained as a Liesegang phenomenon [13], adopting Ostwald’s supersaturation theory [14]: solute depletion at the precipitation front periodically arrests the nucleation process followed by recovery of supersaturation by subsequent diffusion. Although Kirkaldy and others developed a more general model for the spontaneous evolution of spatiotemporal patterns [15, 16], we will follow Wagner’s and Ostwald’s line of reasoning [17] to show that the phenomenon found by us are related to the Liesegang mechanism. In explaining the observed morphology in Ag/Ti-foil/Si couples we should, however, keep in mind that in the present system, contrary to the classical Liesegang phenomena, the “inert” matrix phase (in which precipitation takes place, in our case silver) itself grows as a new phase during the reaction.

The appearance of the silver layer between Ti₅Si₄ and TiAg (Figs. 10d, 11b) creates a situation in which silicon atoms and titanium atoms (from TiAg, note depletion of the grain boundaries in Fig. 11d) can diffuse from opposite directions into the “inert” Ag-solvent and react to form titanium silicide inside the silver (somewhat similar to the Ti/Ag-foil/Si couple shown in Fig. 8). This reaction takes place close to the TiAg-side when the solubility product of the silicide reaches a critical supersaturation value. The internal reaction creates a band of precipitates (Fig. 10e). Probably first Ti₅Si₄ will form, because this phase is, according to the experimentally determined phase diagram, Fig. 5, in equilibrium with nearly the whole range of Ag (Ti) solid solution. As precipitation continues, the silver layer grows at the expense of the dissociating TiAg. The increasing distance between the Ag/TiAg interface and the precipitation zone will cause the flux of Ti to decrease. This will lead to depletion of Ti and since the silicon flux keeps at a practically constant level, the Ti₅Si₄ precipitates will transform into a band of Ti₃Si₂. This first band is shown in Fig. 11c, which is the enlarged area C of Fig. 11a. Subsequently Si can diffuse further into the freshly formed silver layer and the whole process will repeat, forming distinct bands inside the reaction zone, as is shown schematically in Fig. 10f and as observed in Fig. 11d. In the latter micrograph 6 bands are seen to have formed, of which the “youngest” is still very thin. Later on the bands of Ti₅Si₄ can be converted into Ti₃Si₂ and finally into TiSi₂ (Fig. 9d). The process keeps going until the entire layer of TiAg is converted in titanium silicides and silver.

If this mechanism is valid, a same type of periodic structure can be expected for a diffusion couple of the type TiAg/Si (Fig. 12). It was technically difficult to prepare a pure
TiAg compound as a starting material, therefore the experiment was performed in the following manner: a Ti/Ag diffusion couple was annealed in order to form a layer of TiAg and afterwards a slice of silicon was joined to the cross-section of this couple. Between the silicon and the TiAg indeed alternating bands of silver and Ti-silicides were formed.

4 Concluding Remarks

No ternary phases are found in the phase diagram Ag–Ti–Si at 1123 K. A characteristic feature of this system is that all Ti-silicides except Ti₅Si are in equilibrium with pure Ag. Virtually no silver dissolves in the titanium silicides and no solubility of Si in the intermetallic compounds TiAg and Ti₂Ag was found.

The periodic layered morphology in the “sandwich” couple Ag/Ti₅Si/Si is unusual. The phenomenon is explained as the result of an internal reaction of counterdiffusing Ti and Si atoms within the Ag-layer formed inside the transition zone during solid state interaction. The mechanism is similar to that of the formation of Liesegang bands. Our explanation resembles that of Kao and Chang [8], the main difference being that they predict the formation of
We would like to underline that the here discussed spatiotemporal patterns have a different origin than the resembling structures discussed in earlier papers on the systems Fe₃Si/Zn [18], Co₂Zn₁₁[19], Ni/SiC [20] and the systems Pt/SiC and Ni₅Co₂Fe₃Mg [21]. In the latter morphologies supersaturation cannot be a relevant parameter as has been clearly demonstrated. In these cases, cracking of bands as a result of unequal intrinsic diffusion fluxes (Kirkendall effect) has been shown to be the most likely mechanism responsible for the periodic structures.

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Literature


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