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Beek, van, J.A.; Kodentsov, A.; van Loo, F.J.J.

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Phase relations in the Ag–Fe–Ti system at 1123 K

J.A. van Beek, A.A. Kodentsov, F.J.J. van Loo

Eindhoven University of Technology, Laboratory of Solid State Chemistry and Materials Science, TVM-CTK, PO Box 513, 5600 MB Eindhoven, Netherlands

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Abstract

Phase equilibria in the Ag–Fe–Ti system at 1123 K were determined by using polyphase diffusion couples and equilibrated alloys. The experimental observations are in agreement with a thermodynamic evaluation performed on this system. No ternary phases are present on the Ag–Fe–Ti isotherm at 1123 K. The solubility of iron in the binary intermetallic compounds Ti₂Ag and TiAg as well as the solubility of silver in Fe₂Ti are negligible. The maximum silver content in FeTi was estimated as ≈0.5 at.%, while nearly 6 at.% of silver can be dissolved in the β-Ti(Fe) based solid solution at this temperature.

Keywords: Ag–Fe–Ti phase diagram; Diffusion couples

1. Introduction

The ternary system Ag–Fe–Ti is of considerable practical importance because Ag–Ti binary alloys are widely used as a base for commercial active filler metals for brazing various materials, including metals and ceramics. It is a part of the technologically important phase diagram of the quaternary Ag–Cu–Ti–Fe system. Knowledge of this system is needed in order to predict the reaction products formed upon brazing iron-based alloys and the further service of the joints at elevated temperatures. The ternary systems Ag–Cu–Ti and Ag–Cu–Fe have been studied intensively [1–4]. Phase equilibria in the Cu–Fe–Ti system at 1123 K were explored in our previous work [5]. However, no reliable experimental work has yet been reported on the Ag–Fe–Ti system.

The present study, therefore, was focused on the investigation of phase equilibria in the Ag–Fe–Ti system at 1123 K.

In order to determine the phase relations in this system, mainly diffusion couples with two-phase end-members were used. The efficiency of this technique in constructing reliable isothermal cross-sections through phase diagrams is higher compared with that when single-phase alloys are used as end-members of the couples.

For the first type of diffusion couple the chance to find interfaces at which three phases are in equilibrium in the reaction zone is much larger. Schematically this procedure is shown in Fig. 1. For example, if a diffusion couple between P and Q is used, the reaction zone after annealing at a specified temperature might show a morphology indicated in Fig. 1(b). From this diffusion couple two three-phase triangles α+μ+T and β+μ+T can be found by microprobe measurements in the “triple” points 1 and 2 respectively.

2. Experimental details

Silver (99.99), iron (99.98) and titanium (99.98) supplied by Goodfellow (UK) were used as the initial materials. A number of binary Fe–Ti, Ti–Ag and ternary Ti–Fe–Ag alloys were prepared in an arc furnace under argon using a non-consumable tungsten electrode. The ingots were remelted five times to improve their homogeneity. The weight loss of the alloys after melting was less than 2 wt.% relative. The specimen were annealed in an electroresistance furnace in evacuated quartz ampoules at 1123 K for 120 h and quenched in water. The temperature was controlled within ±3 °C. The alloy compositions were controlled by electron probe microanalysis (EPMA) and X-ray diffraction (XRD) analysis with a cylindrical texture camera using manganese-filtered FeKα radiation. Phase compositions of the binary alloys used in the present study are given in Table 1.

For annealed ingots slices of approximate dimensions of 5×5×1.5 mm³ were cut and their bonding faces were ground and polished to a final finish with 1 μm diamond paste. All samples, before bonding, were
Table 2

<table>
<thead>
<tr>
<th>Phase</th>
<th>Crystal structure</th>
<th>Polarization effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-Ti</td>
<td>cubic, Im3m</td>
<td>no</td>
</tr>
<tr>
<td>α-Ti</td>
<td>hexagonal, P63/mmc</td>
<td>strong</td>
</tr>
<tr>
<td>FeTi</td>
<td>cubic, Fm3m</td>
<td>no</td>
</tr>
<tr>
<td>Fe2Ti</td>
<td>hexagonal, P63/mmc</td>
<td>no</td>
</tr>
<tr>
<td>α-Fe</td>
<td>cubic, Im3m</td>
<td>no</td>
</tr>
<tr>
<td>Ag</td>
<td>cubic, Fm3m</td>
<td>no</td>
</tr>
<tr>
<td>Ti2Ag</td>
<td>tetragonal, I4/mmm</td>
<td>strong</td>
</tr>
<tr>
<td>TiAg</td>
<td>tetragonal, P4/mmm</td>
<td>very strong</td>
</tr>
</tbody>
</table>

alloys and/or formed in the reaction zones of the diffusion couples, can be detected with polarized light microscopy just by their polarization effect. Optically anisotropic phases show distinctly different colours in white polarized light due to reflection pleochroism.

Table 2 shows which phases display a polarization effect.

3. Results and discussion

3.1. Reactions between two-phase Fe–Ti alloys and Ag at 1123 K

The microstructure of the reaction zones in the diffusion couples based on silver and various two-phase binary Fe–Ti alloys are given in Fig. 2.

At the interface in the transition zone between a two-phase alloy with the nominal composition Fe80Ti20 and silver after annealing at 1123 K for 100 h in vacuum, three phases were found in equilibrium: α-Fe-based solid solution (Fe90), Fe2Ti and Ag-based solid solution (Fig. 2(a)). Such a morphology indicates a three-phase equilibrium Fe90 + Fe2Ti + Ag in the Ag–Fe–Ti system at this temperature. No silver was detected in the Fe-based solid solution or in the Fe2Ti inside the diffusion zone. Approximately 0.5 at.% of titanium was found in equilibrium with Fe90 and Fe2Ti at the contact surface. The solubility of iron in silver is very low and could not be determined by EPMA.

A similar type of morphology was observed in the diffusion zone between silver and alloy Fe80Ti20(Fe2Ti + FeTi) after heat treatment under these conditions (Fig. 2(b)).

The intermetallic compounds Fe2Ti and FeTi are in equilibrium with silver within the reaction zone. This implies the three-phase equilibrium Fe2Ti + FeTi + Ag at the Ag–Fe–Ti isotherm at 1123 K. Silver was not detected either in Fe2Ti or in FeTi. No iron is dissolved in the silver solid solution, whereas a titanium con-
3.2. Interaction in the diffusion couple Ti$_{80}$Ag$_{20}$ + Fe at 1123 K

The initial Ti$_{80}$Ag$_{20}$ alloy after annealing at 1123 K and quenching in water is a mixture of Ti$_2$Ag and $\alpha$-Ti (Table 1). After the reaction of this alloy with iron at this temperature continuous layers of the intermetallic compounds Fe$_3$Ti and FeTi were found in the diffusion zone (Fig. 3). Deeper in the alloy a two-phase layer $\beta$-Ti + TiAg was formed and, again, no iron was detected in TiAg particles in contact with the layer of FeTi, while nearly 2.0 at.% of silver and about 14.0 at.% of iron were measured in the $\beta$-Ti matrix close to the FeTi layer. The $\beta$-Ti matrix is also a constituent of the next two-phase layer $\beta$-Ti + Ti$_2$Ag adjacent to the starting two-phase Ti–Ag alloy. The composition of the $\beta$-Ti-based solid solution in equilibrium with intermetallic compounds Ti$_2$Ag and TiAg inside the diffusion zone was determined as Ti$_{44.0}$Fe$_{13.5}$Ag$_{2.5}$. Analysis of the morphology of the reaction zone in this diffusion couple shows the three-phase equilibria FeTi + Ti$_2$Ag + $\beta$-Ti, $\beta$-Ti + TiAg + Ti$_2$Ag and $\beta$-Ti + Ti$_2$Ag + $\alpha$-Ti in the Ag–Fe–Ti system at 1123 K.

3.3. Thermodynamic consideration of the Ag–Fe–Ti system

The correctness of the phase equilibria determined with the diffusion couple technique can be checked easily by the simple thermodynamic assessment of the Ag–Fe–Ti system at 1123 K. The latest evaluation of the Ag–Ti system was used in the present work [6,7]. Values for the Gibbs energy of formation of the intermetallic compounds in binary Fe–Ti system were taken from Ref. [8]. All intermetallic phases in the ternary Ag–Fe–Ti system were treated as line com-
pounds. Thermodynamic parameters for the \( \beta \)-Ti-based solid solution (for the sake of simplicity the saturation composition of this phase was assumed to be \( \text{Fe}_2\text{Ti}_9 \)) were evaluated with the subregular solution model. Free energies of formation for different compounds of the Ag-Fe-Ti system used are given in Table 3. A number of possible reactions in the Ag-Fe-Ti system at 1123 K can be written as follows:

\[
\begin{align*}
7\text{Ag} + \text{Fe}_2\text{Ti}_9 &= 2\text{FeTi} + 7\text{TiAg} & (1) \\
\text{Fe}_2\text{Ti} + \text{TiAg} &= 2\text{FeTi} + \text{Ag} & (2) \\
2\text{FeTi} + 7\text{Ti}_2\text{Ag} &= \text{Fe}_2\text{Ti}_9 + 7\text{TiAg} & (3) \\
2\text{Fe} + \text{TiAg} &= \text{Fe}_2\text{Ti} + \text{Ag} & (4)
\end{align*}
\]

with \( \Delta G_R^\circ \) values of \(-6.0\), \(-6.7\), \(-12.2\) and \(-70.7\) kJ respectively. Negative values of the \( \Delta G_R^\circ \) imply that equilibria 1, 2, 3 and 4 in Fig. 4 are impossible. It can be seen that experimental results on Ag-Fe-Ti are in agreement with the thermodynamic predictions.

### Table 3

Free energies of formation for different compounds of the Ag-Fe-Ti system at 1123 K

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \Delta G_R^\circ ) (kJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiAg</td>
<td>-3.4</td>
</tr>
<tr>
<td>Ti_2Ag</td>
<td>-4.2</td>
</tr>
<tr>
<td>Fe_Ti</td>
<td>-74.1</td>
</tr>
<tr>
<td>FeTi</td>
<td>-42.1</td>
</tr>
<tr>
<td>( \beta )-Ti(Fe_2Ti_9)</td>
<td>-102.0</td>
</tr>
</tbody>
</table>

3.4. Stability of \( \alpha \)- and \( \beta \)-Ti-based solid solutions in the ternary Ag-Fe-Ti system at 1123 K

The last question to be clarified is the coexistence of the \( \alpha \)- and \( \beta \)-Ti structures at this isotherm. It can be seen from the binary Ti-Ag and Fe-Ti phase diagrams [9] that a small amount of silver stabilizes the hexagonal \( \alpha \)-Ti structure. Conversely, the presence of iron increases the stability of the b.c.c. \( \beta \)-Ti-based solid solution.

Alloys with a nominal composition \( \text{Ag}_2\text{Fe}_2\text{Ti}_{96} \) and \( \text{Ag}_3\text{Fe}_2\text{Ti}_{93} \) after annealing at 1123 K for 120 h in vacuum and quenching exhibit a morphology shown in Fig. 5. Quite large particles of \( \alpha \)-Ti, which can be identified with polarized light microscopy, are separated by areas with a relatively fine structure based on a titanium solid solution. Such a microstructure can be attributed to the fact that at 1123 K these two alloys consist of two phases based on \( \alpha \)- and \( \beta \)-Ti. However, \( \beta \)-Ti was transformed into the \( \alpha \) structure upon cooling.

Iron was not detected inside the original grains of \( \alpha \)-Ti, while the silver content in \( \alpha \)-Ti was found to be equal to approximately 1.0 and 3.0 at.% for alloys \( \text{Ag}_2\text{Fe}_2\text{Ti}_{96} \) and \( \text{Ag}_3\text{Fe}_2\text{Ti}_{93} \), respectively. It is necessary to realize that the exact position of the \( \beta \)-Ti boundary in the Ag-Fe-Ti system at 1123 K cannot be determined by concentration measurements in the areas of the samples exhibiting a transformation structure after cooling. However, based on the results obtained insight can be gained on the direction of the tie-lines in the two-phase region \( \alpha \)-Ti + \( \beta \)-Ti on this isotherm.

No original particles of \( \alpha \)-Ti were found in the alloy \( \text{Ag}_3\text{Fe}_2\text{Ti}_{90} \) after heat treatment under the same conditions and quenching. Only a typical transformation structure was observed. This underlines that the alloy with this composition lies inside of single-phase \( \beta \)-Ti region at 1123 K.
These observations seem to be confirmed by the morphology of the reaction zone in the diffusion couples based on two-phase ($\alpha$-Ti + $\beta$-Ti) alloy and iron (e.g. Ag$_5$Fe$_2$Ti$_3$ + Fe). The microstructure of this transition zone after annealing at 1123 K for 120 h and quenching is given in Fig. 6. The formation of very thin continuous layers of Fe$_2$Ti and FeTi was found at the interface (these layers cannot be seen on the present micrograph). Next to that a layer of untransformed $\beta$-Ti (Fe, Ag) solid solution was formed. Deeper in the alloy a quite thick layer with a “Widmanstätten”-type structure was clearly visible after etching. Originally, this layer was a $\beta$-Ti-based solid solution, which was transformed into the $\alpha$-Ti structure upon cooling.

Similarly, the $\beta$-Ti-based solid solution present in the initial two-phase ternary alloy was converted into $\alpha$-Ti, which is revealed as the areas with a fine structure separating the original grains of $\alpha$-Ti. Obviously, parts of the $\beta$-Ti solid solution can be retained during quenching, especially the Fe-rich part; retained $\beta$-Ti can be distinguished from $\alpha$-Ti by the absence of polarizing effects in light microscopy.

Finally, the isothermal cross-section through the ternary Ag–Fe–Ti diagram at 1123 K determined in the present study is given in Fig. 7.

4. Concluding remarks

The utility of the polyphase diffusion couples for constructing isothermal cross-sections through ternary phase diagrams was demonstrated. It turned out to be possible, by investigating relatively few such diffusion couples, to construct a large part of the Ag–Fe–Ti phase diagram at 1123 K.

No ternary phases are present in the Ag–Fe–Ti system at 1123 K. Experimentally determined phase equilibria were confirmed by thermodynamic consideration of this ternary system.

Additives of silver in titanium stabilize the $\alpha$-Ti structure, whereas the presence of Fe in titanium-based solid solution has the opposite effect. A maximum of about 6 at.% of silver can be dissolved in the $\beta$-Ti (Fe) based solid solution.

It is typical for Ag–Fe–Ti as well as for Cu–Fe–Ti [5] isotherms at 1123 K that the Ag- or Cu-based solid solution can be in equilibrium with the $\alpha$-Fe-based solid solution and the intermetallic compounds Fe$_2$Ti or FeTi. When Ag–Ti active filler metals are used for brazing iron the reaction products (Fe-based solid solution or intermetallic phases) which will form inside the brazing seam during the brazing procedure and the further high-temperature exposure of the joint entirely depend on the activity of titanium in the brazing alloy. When brazing iron-based alloys, other reaction products containing a foreign element might develop as well.

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References


