Substitutional and Interstitial Diffusion in $\alpha_2$-$\text{Ti}_3\text{Al(O)}$

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The reaction between $\text{Al}_2\text{O}_3$ and $\alpha_2$-$\text{Ti}_3\text{Al}$ was studied with a series of $\text{Al}_2\text{O}_3/\alpha_2$-$\text{Ti}_3\text{Al}$ multiphase diffusion couples annealed at 900, 1000 and 1100°C. The diffusion-paths were found to strongly depend on $\alpha_2$-$\text{Ti}_3\text{Al(O)}$ composition. For alloys with low oxygen concentrations the reaction involved the reduction of $\text{Al}_2\text{O}_3$, the formation of a $\gamma$-$\text{TiAl}$ reaction-layer and diffusion of Al and O into the $\alpha_2$-$\text{Ti}_3\text{Al}$ substrate. Measured concentration profiles across the interaction-zone showed “up-hill” diffusion of O in $\alpha_2$-$\text{Ti}_3\text{Al(O)}$ indicating a significant thermodynamic interaction between O and Al, Ti or both. Diffusion coefficients for the interstitial O in $\alpha_2$-$\text{Ti}_3\text{Al(O)}$ were determined independently from the interdiffusion of Ti and Al on the substitutional lattice. Diffusion coefficients are reported for $\alpha_2$-$\text{Ti}_3\text{Al(O)}$ as well a $\gamma$-$\text{TiAl}$. Interpretation of the results were aided with the subsequent measurement of the activities of Al, Ti and O in $\alpha_2$-$\text{Ti}_3\text{Al(O)}$ by Knudsen effusion-cell mass spectrometry.
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Al₂O₃ only oxide in equilibrium with α₂-Ti₃Al + γ-TiAl, but…
both phases must be saturated with O
outline

• rationale… possible MMC and oxidation of $\alpha_2$-Ti$_3$Al + $\gamma$-TiAl

• multi-phase couples: $\alpha_2 / \text{Al}_2\text{O}_3$
  → results & calculations

• single-phase couples: $\alpha_2(\text{O}) / \alpha_2(\text{O})$
  → results & calculations

• partial thermodynamic properties in $\alpha_2$-Ti$_3$Al(O)

• summary
multi-phase Ti-Al / Al₂O₃ couples

- arc-melted: Al, Ti & TiO₂; annealed at \( T = 900, 1000, 1100^\circ\text{C} \)
  - closed system: Ta-foil (barrier for SiO)- in SiO₂ capsule
- HIP bonding (170 MPa, 1100ºC for 2 h), poly-crystalline Al₂O₃
  - re-encapsulated, reacted 900, 1000, 1100ºC for \( t = 20 \sim 500 \text{ h} \)
- analysis: metallography, optical, EPMA and micro-hardness

<table>
<thead>
<tr>
<th>alloy</th>
<th>comp. (at.%)</th>
<th>phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 ~ 3</td>
<td>Ti-(49, 52, 55)Al</td>
<td>( \gamma)-TiAl</td>
</tr>
<tr>
<td>4</td>
<td>Ti-25Al</td>
<td>( \alpha_2)-Ti₃Al</td>
</tr>
<tr>
<td>5</td>
<td>Ti-32Al</td>
<td>( \alpha_2)-Ti₃Al</td>
</tr>
<tr>
<td>6</td>
<td>Ti-35Al</td>
<td>( \alpha_2)-Ti₃Al</td>
</tr>
<tr>
<td>7</td>
<td>Ti-33.35Al-5O</td>
<td>( \alpha_2)-Ti₃Al(O)</td>
</tr>
<tr>
<td>8</td>
<td>Ti-27Al-10O</td>
<td>( \alpha_2)-Ti₃Al(O)</td>
</tr>
<tr>
<td>9 ~ 10</td>
<td>Ti-(40, 48)Al</td>
<td>( \alpha_2 ) + ( \gamma )</td>
</tr>
</tbody>
</table>
α₂-Ti₃Al / Al₂O₃ couples

Ti-32Al / Al₂O₃,

$\alpha_2$-Ti₃Al / Al₂O₃ couples

Al₂O₃

γ-TiAl

$\alpha_2$-Ti₃Al

1100ºC  1000ºC  900ºC

marker

Ti-32Al / Al₂O₃,

t = 500 h
$\alpha_2$-Ti$_3$Al / Al$_2$O$_3$ couples

$T = 1100^\circ$C

$\text{Al}_2\text{O}_3 = 2\text{Al}_{\gamma,\alpha_2} + 3\text{O}_{\gamma,\alpha_2}$ … “gas / solid”

Al, O supplied at activity of $\gamma$ / Al$_2$O$_3$

$\mathcal{J}_O \gg \mathcal{J}_A$ (from diffusion path)

$\mathcal{J}_O \to$ through $\gamma$-layer into $\alpha_2(O)$

$\mathcal{J}_A \to \gamma$-layer growth and enriches $\alpha_2(O)$

“up-hill” diffusion of O in $\alpha_2(O)$

$\mathcal{J}_O$ from low to high $X_O$:  

$\mathcal{J}_O = -\mathcal{D}_{O\alpha} \frac{\partial C_O}{\partial x} - \mathcal{D}_{O\text{Al}} \frac{\partial C_{\text{Al}}}{\partial x}$

$\mathcal{D}_{O\text{Al}}$ must be +ve and significant…

+ve thermodynamic interaction between O and Ti + Al

EPMA error, TiO$_2$-layer
treating diffusion in Ti-Al-O

- Ti and Al substitutional; O interstitial, but [OTi₆] only stable sites
- limited kinetic interaction between lattices plus \( \bar{J}_O \gg \bar{J}_Al \), treat:
  - Ti-Al “pseudo binary” and O “transient equilibrium”

\[ \alpha_2 \text{-Ti}_3\text{Al (DO}_{19}\text{)} \quad \gamma \text{-TiAl (L1}_{0}\text{)} \]

- correct profiles: \( r(\text{Ti, Al}) = 1.45, 1.43\text{Å} \); \( V_m(\alpha_2, \gamma) \approx 10.0 \text{ cm}^3\text{mol}^{-1} \)

\[ C_i = (N_i/(N_{\text{Ti}} + N_{\text{Al}}))/V_m \]

\[ C_O = N_O/V_m \]

**concentration profiles**

\[ \text{Al}_2\text{O}_3 / \text{Ti-25Al} \]

\[ T = 1100^\circ\text{C}, 250 \text{ h} \]

**raw EPMA data**

- Ti and Al aren’t diffusing!
- “up-hill” diffusion of O

**EPMA error, TiO\textsubscript{2}-layer**

**corrected profile**

\[ C_i = \frac{N_i}{(N_{Ti} + N_{Al})}/V_m \]

\[ C_O = \frac{N_O}{V_m} \]
\( \tilde{D}(N_i) \) in \( \alpha_2\)-Ti\(_3\)Al and \( \gamma\)-TiAl

\[
\begin{array}{|c|c|c|}
\hline
\text{Alloy} & \tilde{D}_\gamma \quad (\text{cm}^2\text{sec}^{-1}) & \tilde{D}_\alpha \quad (\text{cm}^2\text{sec}^{-1}) \\
\hline
1100^\circ C & & \\
\text{Ti-25Al} & 9.9\pm0.5\times10^{-11} & 2.7\pm0.3\times10^{-12} \\
\text{Ti-32Al} & 6.3\pm0.6\times10^{-11} & 3.0\pm1.5\times10^{-12} \\
\text{Ti-35Al} & 5.4\pm0.3\times10^{-11} & 5.2\pm1.3\times10^{-12} \\
\text{Ti-33.3Al-5O} & 6.1\pm0.7\times10^{-11} & 1.2\pm0.2\times10^{-12} \\
\hline
1000^\circ C & & \\
\text{Ti-25Al} & 2.8\pm0.4\times10^{-11} & 2.6\pm0.5\times10^{-13} \\
\text{Ti-32Al} & 5.9\pm0.9\times10^{-11} & 3.3\pm0.7\times10^{-13} \\
\hline
900^\circ C & & \\
\text{Ti-25Al} & 5.1\pm2.0\times10^{-12} & 3.4\pm0.9\times10^{-14} \\
\text{Ti-32Al} & 1.4\pm0.5\times10^{-11} & 3.9\pm1.0\times10^{-14} \\
\hline
\end{array}
\]

average values
Arrhenius behavior / comparison

\[ \alpha_2 - \text{Ti}_3\text{Al} \]

\[ \gamma - \text{TiAl} \]
interstitial diffusion of O in $\alpha_2$-Ti$_3$Al

- $J_0 > J_{(Al,Ti)}$... “transient equilibrium” (Kirkaldy et al. 1958-64)
  O, local equilibrium; redistributes with Ti-Al substitutional lattice

\[
\tilde{J}_i = -D_{OO} \frac{\partial C_O}{\partial x} - D_{OAl} \frac{\partial C_{Al}}{\partial x} \approx 0
\]

- predict interdiffusion coefficient ratio:

\[
\frac{D_{OAl}}{D_{OO}} = -\frac{\Delta C_O}{\Delta C_{Al}}
\]

\[T = 1100^\circ C\]

\[\tilde{D}_{OAl} / \tilde{D}_{OO} = 0.44 \pm 0.08\]
calculated $\tilde{D}_{OO}$

- $\tilde{J}_O^i = -\tilde{D}_{OO}^T \frac{\partial C_O}{\partial x} - \tilde{D}_{OA}^T \frac{\partial C_{Al}}{\partial x}$, no intersecting diffusion paths...
- region of pure O enrichment, $\frac{\partial C_{Al}}{\partial x} = 0 \Rightarrow \tilde{J}_O^i = -\tilde{D}_{OO}^T \frac{\partial C_O}{\partial x}$
- EPMA and micro-hardness; assume $\tilde{D}_{OO}$ const.

\[
\frac{C(x,t) - C_s}{C_O - C_s} = erf\left(\frac{x}{2\sqrt{Dt}}\right)
\]

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$\tilde{D}_{OO}^T$ ($10^{-10}$cm$^2$s$^{-1}$)</th>
<th>Arrenheinus Behaviour</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1100°C</td>
<td>1000°C</td>
</tr>
<tr>
<td>II(Ti-25Al)</td>
<td>4.0±1.0</td>
<td>0.75±0.15</td>
</tr>
<tr>
<td>II(Ti-32Al)</td>
<td>5.5±1.5</td>
<td>0.6±0.15</td>
</tr>
<tr>
<td>III(Ti-35Al)</td>
<td>6.5±1.5</td>
<td>1.0±1.5</td>
</tr>
</tbody>
</table>

$\tilde{D}_{OO} / \tilde{D}_{Al} = 100 \sim 1000$
single-phase $\alpha_2$($O$) / $\alpha_2$($O$) couples

- arc-melted pure-Al, Ti & TiO$_2$, annealed in closed system:
  - Ta-foil in SiO$_2$ capsule
- uni-axial hot press (1100°C for 2 ~ 4 h); $T = 1100°C$ for 100 h
- analysis: metallography, optical & EPMA
  - used multi-alloy EPMA standard... TiO$_2$ surface-layer

<table>
<thead>
<tr>
<th>alloy</th>
<th>comp. (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ti-25.8Al-0.1O</td>
</tr>
<tr>
<td>2</td>
<td>Ti-29.6Al-0.3O</td>
</tr>
<tr>
<td>3</td>
<td>Ti-33.6Al-0.1O</td>
</tr>
<tr>
<td>4</td>
<td>Ti-24.7Al-3.9O</td>
</tr>
<tr>
<td>5</td>
<td>Ti-28.5Al-4.0O</td>
</tr>
<tr>
<td>6</td>
<td>Ti-32.0Al-3.9O</td>
</tr>
<tr>
<td>7</td>
<td>Ti-23.5Al-7.7O</td>
</tr>
<tr>
<td>8</td>
<td>Ti-28.0Al-7.7O</td>
</tr>
<tr>
<td>9</td>
<td>Ti-31.1Al-7.8O</td>
</tr>
</tbody>
</table>
constant Ti / Al ratio

$T = 1100^\circ C, 100 \text{ h}$

$\frac{\text{Ti}}{\text{Al}} \approx 2.9, 2.3, 2.0$

$\mathcal{J}_o = -\frac{\partial C_0}{\partial x} - \frac{\partial C_{Al}}{\partial x}$

$\mathcal{J}_o = -\frac{\partial C_0}{\partial x}$

$x_m - x_o = 186\mu m$

$x_m - x_o = 109\mu m$

$x_m - x_o = 173\mu m$
calculated $J_0$ and $\tilde{D}_{OO}$

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig.png}
\end{figure}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
alloy & $\tilde{D}_{OO}$ (10^{-10}cm^2/s) $T = 1100^\circ$C & Ti / Al (couple) & $\tilde{D}_{OO}$ (10^{-10}cm^2/s) $T = 1100^\circ$C \\
\hline
Ti-25Al & 4.0±1.0 & 2.9 (7 / 1) & 4.8±1.0 \\
Ti-32Al & 5.5±1.5 & 2.3 (8 / 2) & 6.2±1.5 \\
Ti-35Al & 6.5±1.5 & 2.0 (9 / 3) & 6.1±2.0 \\
\hline
\end{tabular}
\end{table}

$\tilde{D}_{OO} \sim$ independent of $X_O$ but small Ti / Al dependence (?)
constant $C_O$

$T = 1100^\circ C, 100$ h

- profiles flipped relative to diffusion path
- classic “up-hill” profile for O...
  - thermodynamic interaction: Ti-Al $\rightarrow$ O
- Ti-Al interaction zone decreases with $X_O$
  - $O \rightarrow$ Ti-Al: kinetic / thermodynamic ?
  - expect similar $\Delta \mu_{(Ti,Al)}$ for each $X_O$
calculated $\tilde{J}_{\text{Al}}$ and $\tilde{D}_{\text{Al}}$

- Ti-Al and O diffusion isn’t independent
- $X_O$ not controlled in previous studies:
  - Sprengel: SiO$_2$ capsules, no Ta-foil
  - Rusing: flowing Ar-atmosphere
“intersecting” paths: 9-1, 7-3, 6-4

- 9-1 and 7-3 don’t intersect; 7-3 and 6-4 are parallel…
  ¬ new couples needed to determine kinetic interaction $O \rightarrow Ti-Al$
- 9-1 diffusion path shows “up-hill” Al diffusion:
  ¬ $O$ dissolution must: increase $a(Al)$, decrease $a(Ti)$ (or both)

\[
\tilde{J}^i_O = -\tilde{D}^{Ti}_{OO} \frac{\partial C_O}{\partial x} - \tilde{D}^{Ti}_{OAl} \frac{\partial C_{Al}}{\partial x}
\]

\[
\tilde{J}^i_{Al} = -\tilde{D}^{Ti}_{AlO} \frac{\partial C_O}{\partial x} - \tilde{D}^{Ti}_{AlAl} \frac{\partial C_{Al}}{\partial x}
\]
thermodynamic measurements

multi-cell KEMS

pressure measurement

\[ p(i) = I_{ik}^+ T / S_{ik} \]

activity measurement

\[ a(i) = \frac{p(i)}{p^*(i)} = \frac{I_i}{I_i^*} \]

\[ a(i) = \frac{p(i)}{p^*(Au)} \cdot \left[ \frac{p^*(Au)}{p^*(i)} \right] = \frac{I_i}{I_{Au}^*} \cdot \frac{S_{Au}}{S_i^*} \cdot \frac{g(R)}{g(A)} \cdot \left[ \frac{p^*(Au)}{p^*(i)} \right] \]

\( i = \text{Ti, Al, Al}_2\text{O} \)
$a(\text{Al})$ vs. $X_O$

$T(°C)$

$1500$ $1400$ $1300$ $1200$ $1100$ $1000$

$1$ $0.1$ $0.01$ $0.001$

$10^4/T (K^{-1})$

$5.5$ $6.0$ $6.5$ $7.0$ $7.5$ $8.0$

reference state: $\{\text{Al}(l) + \text{Al}_2\text{O}_3(s)\}$
$\alpha$(Ti) vs. $X_0$

Increasing $O$

$T(\circ C)$ vs. $10^4/T (K^{-1})$

Ti-30Al  
Ti-28Al-4O  
Ti-28Al-7.9O  
Ti-35Al-20O

reference state: $\{Ti(s) + Y_2O_3(s)\}$
• $\alpha_2 / Al_2O_3$ and $\alpha_2(O) / \alpha_2(O)$ couples… Ti-Al-O reaction behavior
• unsaturated $\alpha_2(O)$ reduces $Al_2O_3$: $\gamma$-layer, “up-hill” $\tilde{J}_O$ in $\alpha_2(O)$
• $\tilde{J}_O \gg \tilde{J}_{Al}$; treat subst. and interstitial lattices independently
  - Ti-Al “pseudo binary” $\tilde{D} = \tilde{D}(C_i)$, scatter in data (effect of $X_O$)
  - “transient equ.”: $\tilde{D}_{OAl} / \tilde{D}_{OO}$ and $\tilde{D}_{OO}$, slight Ti / Al dependence
• $\alpha_2(O) / \alpha_2(O)$ couples: confirm $\tilde{D}_{OAl} / \tilde{D}_{OO}$ and $\tilde{D}_{OO}$ behavior,
  but Ti-Al interdiffusion reduced > 10x with $X_O 0.005 \rightarrow 0.08$
  - thermodynamic interaction + change in mobility (?)
  - difficult to observe kinetic aspect; thermodynamics is clear
• more work is need…
  - significant insight to oxidation of Ti-Al alloys

summary
acknowledgements:

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