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

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

$T = 1000^\circ C$

$\text{Al}_2\text{O}_3$ only oxide in equilibrium with $\alpha_2$-$\text{Ti}_3\text{Al} + \gamma$-$\text{TiAl}$, 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: $\alpha_2$ / Al$_2$O$_3$
  ⇐ results & calculations

• single-phase couples: $\alpha_2$(O) / $\alpha_2$(O)
  ⇐ results & calculations

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

• summary
multi-phase Ti-Al / Al$_2$O$_3$ couples

- arc-melted: Al, Ti & TiO$_2$; annealed at $T = 900, 1000, 1100^\circ$C
  - closed system: Ta-foil (barrier for SiO)- in SiO$_2$ capsule
- HIP bonding (170 MPa, 1100$^\circ$C for 2 h), poly-crystalline Al$_2$O$_3$
  - re-encapsulated, reacted 900, 1000, 1100$^\circ$C for $t = 20 \sim 500$ 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>$\alpha_2$-Ti$_3$Al</td>
</tr>
<tr>
<td>5</td>
<td>Ti-32Al</td>
<td>$\alpha_2$-Ti$_3$Al</td>
</tr>
<tr>
<td>6</td>
<td>Ti-35Al</td>
<td>$\alpha_2$-Ti$_3$Al</td>
</tr>
<tr>
<td>7</td>
<td>Ti-33.35Al-5O</td>
<td>$\alpha_2$-Ti$_3$Al(O)</td>
</tr>
<tr>
<td>8</td>
<td>Ti-27Al-10O</td>
<td>$\alpha_2$-Ti$_3$Al(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**

- **Al₂O₃**
- **γ-TiAl**
- **α₂-Ti₃Al**

**Marker**

Ti-32Al / Al₂O₃,

\[ t = 500 \text{ h} \]

---

**Graph**

- **1100°C**
- **1000°C**
- **900°C**

**Thickness (μm)**

- \[ k_p = 4.0 \pm 0.2 \]
- \[ k_p = 0.72 \pm 0.04 \]
- \[ k_p = 0.12 \pm 0.02 \]

**Sqrt. Time (10⁻² s⁻¹)**

**k_p (10¹¹ cm² s⁻¹)**
\( \alpha_2 \text{-Ti}_3\text{Al} / \text{Al}_2\text{O}_3 \) couples

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

Al, O supplied at activity of \( \gamma / \text{Al}_2\text{O}_3 \)

\( \tilde{J}_O >> \tilde{J}_\text{Al} \) (from diffusion path)

\( \tilde{J}_O \rightarrow \) through \( \gamma \)-layer into \( \alpha_2(\text{O}) \)

\( \tilde{J}_\text{Al} \rightarrow \gamma \)-layer growth and enriches \( \alpha_2(\text{O}) \)

“up-hill” diffusion of O in \( \alpha_2(\text{O}) \)

\( T = 1100^\circ \text{C} \)

\( \tilde{J}_O \) from low to high \( X_O \):

\[
\tilde{J}_O = -\tilde{D}_{O\text{O}}^{\text{Ti}} \frac{\partial C_O}{\partial x} - \tilde{D}_{O\text{Al}}^{\text{Ti}} \frac{\partial C_{\text{Al}}}{\partial x}
\]

\( \tilde{D}_{O\text{Al}}^{\text{Ti}} \) must be +ve and significant...

+ve thermodynamic interaction between O and Ti + Al

EPMA error, TiO\(_2\)-layer
treated diffusion in Ti-Al-O

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

\[
\begin{align*}
\alpha_2\text{-Ti}_3\text{Al (DO}_{19}\text{)} & \\
\gamma\text{-TiAl (L}_{10}\text{)}
\end{align*}
\]

- correct profiles: \( r(\text{Ti, Al}) = 1.45, 1.43\text{Å} \); \( V_m(\alpha_2, \gamma) \approx 10.0 \text{ cm}^3\text{mol}^{-1} \)
  - Ti, Al: \( C_i = \frac{N_i}{(N_{\text{Ti}} + N_{\text{Al}})} / V_m \)
  - O: \( C_O = \frac{N_O}{V_m} \)

concentration profiles

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

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

“up-hill” diffusion of O

raw EPMA data

EPMA error, TiO$_2$-layer

$\gamma$-TiAl
$\alpha_2$-Ti$_2$Al(O)

Ti and Al aren’t diffusing!

corrected profile

$C_i = \left( N_i / (N_{Ti} + N_{Al}) \right) / V_m$

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

![Graph showing interdiffusivity values for different alloys at 900°C, 1000°C, and 1100°C.]

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$\tilde{D}_\gamma$ (cm$^2$sec$^{-1}$)</th>
<th>$\tilde{D}_{\alpha_2}$ (cm$^2$sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-25Al</td>
<td>$9.9\pm0.5\times10^{-11}$</td>
<td>$2.7\pm0.3\times10^{-12}$</td>
</tr>
<tr>
<td>Ti-32Al</td>
<td>$6.3\pm0.6\times10^{-11}$</td>
<td>$3.0\pm1.5\times10^{-12}$</td>
</tr>
<tr>
<td>Ti-35Al</td>
<td>$5.4\pm0.3\times10^{-11}$</td>
<td>$5.2\pm1.3\times10^{-12}$</td>
</tr>
<tr>
<td>Ti-33.3Al-5O</td>
<td>$6.1\pm0.7\times10^{-11}$</td>
<td>$1.2\pm0.2\times10^{-12}$</td>
</tr>
<tr>
<td>Ti-25Al</td>
<td>$2.8\pm0.4\times10^{-11}$</td>
<td>$2.6\pm0.5\times10^{-12}$</td>
</tr>
<tr>
<td>Ti-32Al</td>
<td>$5.9\pm0.9\times10^{-11}$</td>
<td>$3.3\pm0.7\times10^{-13}$</td>
</tr>
<tr>
<td>Ti-25Al</td>
<td>$5.1\pm2.0\times10^{-12}$</td>
<td>$3.4\pm0.9\times10^{-14}$</td>
</tr>
<tr>
<td>Ti-32Al</td>
<td>$1.4\pm0.5\times10^{-11}$</td>
<td>$3.9\pm1.0\times10^{-14}$</td>
</tr>
</tbody>
</table>

**Average Values:**

$T = 1100^\circ$C
Arrhenius behavior / comparison

\[ \alpha_2 - Ti_3Al \]

\[ \gamma - TiAl \]

<table>
<thead>
<tr>
<th>( T ) (°C)</th>
<th>( \alpha_2 )</th>
<th>( \gamma )</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D_0 ) (cm²s⁻¹)</td>
<td>( E_a ) (kJmol⁻¹)</td>
<td>( D_0 ) (cm²s⁻¹)</td>
<td>( E_a ) (kJmol⁻¹)</td>
<td></td>
</tr>
<tr>
<td>1169-1366</td>
<td>-</td>
<td>3.0×10⁻³</td>
<td>210</td>
<td>concentration</td>
</tr>
<tr>
<td>845-1310</td>
<td>10</td>
<td>312±6</td>
<td>2.8</td>
<td>295±10</td>
</tr>
<tr>
<td>881-1400</td>
<td>-</td>
<td>1.5</td>
<td>291±10</td>
<td>tracer</td>
</tr>
<tr>
<td>897-995</td>
<td>0.3</td>
<td>290±15</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>897-995</td>
<td>n/a</td>
<td>( \approx 350 )</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>750-1250</td>
<td>1.5×10⁻⁶</td>
<td>117±5</td>
<td>2×10⁻⁵</td>
<td>152±2</td>
</tr>
<tr>
<td>900-1100</td>
<td>0.3</td>
<td>290±25</td>
<td>1.1×10⁻⁵</td>
<td>140±40</td>
</tr>
</tbody>
</table>
interstitial diffusion of O in $\alpha_2$-Ti$_3$Al

- $\tilde{J}_O >> \tilde{J}_{(Al,Ti)}$… “transient equilibrium” (Kirkaldy et al. 1958-64)
  O, local equilibrium; redistributes with Ti-Al substitutional lattice

$$\tilde{J}_O = -\tilde{D}_{OO} \frac{\partial C_O}{\partial x} - \tilde{D}_{OAl} \frac{\partial C_{Al}}{\partial x} \approx 0$$

- predict interdiffusion coefficient ratio:

$$\frac{\tilde{D}_{OAl}}{\tilde{D}_{OO}} = -\frac{\Delta C_O}{\Delta C_{Al}}$$

$T = 1100^\circ C$

$\tilde{D}_{OAl} / \tilde{D}_{OO} = 0.44\pm0.08$
calculated $\tilde{D}_{OO}$

- $\tilde{J}_O^i = -\tilde{D}_{OO}^T \frac{\partial C_O}{\partial x} - \tilde{D}_{OAI}^T \frac{\partial C_{Al}}{\partial x}$, 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.

$$\frac{C(x,t) - C_s}{C_O - C_s} = erf\left(\frac{x}{2\sqrt{D_t}}\right)$$

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$\tilde{D}_{OO}^T$ ($10^{-10}$cm$^2$s$^{-1}$)</th>
<th>Arrehenius Behaviour</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1100°C</td>
<td>1000°C</td>
</tr>
<tr>
<td>I(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>

$\tilde{D}_{OO} / \tilde{D}_{AI} = 100 \sim 1000$
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 (1100ºC for 2 ~ 4 h); $T = 1100$ºC for 100 h
- analysis: metallography, optical & EPMA
  - used multi-alloy EPMA standard... TiO$_2$ surface-layer
constant Ti / Al ratio

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

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

$\bar{J}_0 = -D_{oo}^{Ti} \frac{\partial C_A}{\partial x} - D_{oo}^{Ti} \frac{\partial C_{Al}}{\partial x}$

$\rightarrow \bar{J}_0 = -D_{oo}^{Ti} \frac{\partial C_A}{\partial x}$

$x_m - x_o = 186 \mu m$

$x_m - x_o = 109 \mu m$

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

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

<table>
<thead>
<tr>
<th>alloy</th>
<th>$\tilde{D}_{OO}$ (10$^{-10}$cm$^2$/s) $T = 1100^\circ$C</th>
<th>Ti / Al (couple)</th>
<th>$\tilde{D}_{OO}$ (10$^{-10}$cm$^2$/s) $T = 1100^\circ$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-25Al</td>
<td>4.0±1.0</td>
<td>2.9 (7 / 1)</td>
<td>4.8 ±1.0</td>
</tr>
<tr>
<td>Ti-32Al</td>
<td>5.5±1.5</td>
<td>2.3 (8 / 2)</td>
<td>6.2 ±1.5</td>
</tr>
<tr>
<td>Ti-35Al</td>
<td>6.5±1.5</td>
<td>2.0 (9 / 3)</td>
<td>6.1 ±2.0</td>
</tr>
</tbody>
</table>
constant $C_O$

- 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 $X_O$
- Ti-Al and O diffusion isn't independent
- $X_0$ not controlled in previous studies:
  - Sprengel: SiO$_2$ capsules, no Ta-foil
  - Rusing: flowing Ar-atmosphere

$\tilde{J}_{Al}$ and $\tilde{D}_{Al}$

Calculated $\tilde{J}_{Al}$ and $\tilde{D}_{Al}$
“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 → Ti-Al
- 9-1 diffusion path shows “up-hill” Al diffusion:
  - O dissolution must: increase \( a(\text{Al}) \), decrease \( a(\text{Ti}) \) (or both)

\[
\tilde{J}_O^i = -D_{OO}^{\text{Ti}} \frac{\partial C_O}{\partial x} - D_{OAI}^{\text{Ti}} \frac{\partial C_{\text{AI}}}{\partial x}
\]

\[
\tilde{J}_{\text{Al}}^i = -D_{\text{AlO}}^{\text{Ti}} \frac{\partial C_O}{\partial x} - D_{\text{AlAI}}^{\text{Ti}} \frac{\partial C_{\text{AI}}}{\partial x}
\]
thermodynamic measurements

multi-cell KEMS

pressure measurement

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

activity measurement

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

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

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

$T(°C)$

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

Increasing O

$\alpha_2(O) + \gamma + Al_2O_3$

$\alpha-Ti(Al,O)$

$\alpha_2(O)$

reference state: $\{Al(l) + Al_2O_3(s)\}$
$a(Ti)$ vs. $X_O$

$T(°C)$

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

- $α-Ti(Al,O)$

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

Increasing O

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 \(\alpha_2(O)\)

• \(\tilde{J}_O >> \tilde{J}_{Al}\); treat subst. and interstitial lattices independently
  - Ti-Al “pseudo binary” \(\tilde{D} = \tilde{D}(C_i)\), scatter in data (effect of \(X_0\))
  - “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 \(X_0\) 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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