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.
Substitutional and Interstitial Diffusion in $\alpha_2\cdot Ti_3Al(O)$

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Al$_2$O$_3$ only oxide in equilibrium with $\alpha_2$-Ti$_3$Al + $\gamma$-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 / Al₂O₃ couples

- arc-melted: Al, Ti & TiO₂; annealed at $T = 900, 1000, 1100^\circ$C
  - closed system: Ta-foil (barrier for SiO)- in SiO₂ capsule
- HIP bonding (170 MPa, 1100°C for 2 h), poly-crystalline Al₂O₃
  - re-encapsulated, reacted 900, 1000, 1100°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>$\alpha_2$-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>
$\alpha_2$-Ti$_3$Al / Al$_2$O$_3$ couples

Ti-32Al / Al$_2$O$_3$, $t = 500$ h

$\alpha_2$-Ti$_3$Al

$\gamma$-TiAl

$\text{Al}_2\text{O}_3$

marker

1100°C  1000°C  900°C

$\sqrt{\text{time (10^{-2}s^{1/2})}}$

$\text{thickness (\mu m)}$

$k_p(10^{11}\text{cm}^2\text{s}^{-1})$

$\text{sqrt. time (10^{-2}s^{1/2})}$

$kp = 4.0 \pm 0.2$

$kp = 0.72 \pm 0.04$

$kp = 0.12 \pm 0.02$
α₂-Ti₃Al / Al₂O₃ 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 γ / Al₂O₃

\[ \tilde{J}_O \gg \tilde{J}_\text{Al} \text{ (from diffusion path)} \]

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

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

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

\[ \tilde{J}_O \text{ from low to high } X_O: \]

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

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

+ve thermodynamic interaction between O and Ti + Al

\( T = 1100^\circ\text{C} \)
treated diffusion in Ti-Al-O

- Ti and Al substitutional; O interstitial, but [OTi₆] only stable sites
- limited kinetic interaction between lattices plus $\tilde{J}_O >> \tilde{J}_{Al}$, treat:
  - Ti-Al "pseudo binary" and O "transient equilibrium"

\[ \alpha_2\text{-Ti}_3\text{Al (DO}_{19}\text{)} \quad \gamma\text{-TiAl (L1}_{10}\text{)} \]

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

- Ti, Al: $C_i = (N_i/(N_{Ti} + N_{Al}))/V_m$
- O: $C_0 = N_O/V_m$

Al₂O₃ / Ti-25Al

\[ T = 1100°C, \text{ 250 h} \]

concentration profiles

raw EPMA data

“up-hill” diffusion of O

EPMA error, TiO₂-layer

corrected profile

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

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

<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></td>
<td>( T = 1100^\circ)C</td>
<td></td>
</tr>
<tr>
<td>Ti-25Al</td>
<td>9.9±0.5\times10^{-11}</td>
<td>2.7±0.3\times10^{-12}</td>
</tr>
<tr>
<td>Ti-32Al</td>
<td>6.3±0.6\times10^{-11}</td>
<td>3.0±1.5\times10^{-12}</td>
</tr>
<tr>
<td>Ti-35Al</td>
<td>5.4±0.3\times10^{-11}</td>
<td>5.2±1.3\times10^{-12}</td>
</tr>
<tr>
<td>Ti-33.3Al-5O</td>
<td>6.1±0.7\times10^{-11}</td>
<td>1.2±0.2\times10^{-12}</td>
</tr>
<tr>
<td></td>
<td>( T = 1000^\circ)C</td>
<td></td>
</tr>
<tr>
<td>Ti-25Al</td>
<td>2.8±0.4\times10^{-11}</td>
<td>2.6±0.5\times10^{-13}</td>
</tr>
<tr>
<td>Ti-32Al</td>
<td>5.9±0.9\times10^{-11}</td>
<td>3.3±0.7\times10^{-13}</td>
</tr>
<tr>
<td></td>
<td>( T = 900^\circ)C</td>
<td></td>
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<tr>
<td>Ti-25Al</td>
<td>5.1±2.0\times10^{-12}</td>
<td>3.4±0.9\times10^{-14}</td>
</tr>
<tr>
<td>Ti-32Al</td>
<td>1.4±0.5\times10^{-11}</td>
<td>3.9±1.0\times10^{-14}</td>
</tr>
</tbody>
</table>

Average values
### Arrhenius behavior / comparison

#### α₂-Ti₃Al

<table>
<thead>
<tr>
<th>Temperature Range (°C)</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1169-1366</td>
<td>concentration</td>
<td>Kainuma, Inden (1997)</td>
</tr>
<tr>
<td>845-1310</td>
<td>concentration</td>
<td>Sprengel (1996)</td>
</tr>
<tr>
<td>881-1400</td>
<td>tracer</td>
<td>Kroll (1992)</td>
</tr>
<tr>
<td>897-995</td>
<td>tracer</td>
<td>Rüsing, Herzig (1995)</td>
</tr>
<tr>
<td>897-995</td>
<td>concentration</td>
<td>Rüsing, Herzig (1995)</td>
</tr>
<tr>
<td>900-1100</td>
<td>concentration</td>
<td>Present results</td>
</tr>
</tbody>
</table>

#### γ-TiAl

<table>
<thead>
<tr>
<th>Temperature Range (°C)</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>845-1310</td>
<td>concentration</td>
<td>Sprengel (1996)</td>
</tr>
<tr>
<td>881-1400</td>
<td>tracer</td>
<td>Kroll (1992)</td>
</tr>
<tr>
<td>897-995</td>
<td>tracer</td>
<td>Rüsing, Herzig (1995)</td>
</tr>
<tr>
<td>897-995</td>
<td>concentration</td>
<td>Rüsing, Herzig (1995)</td>
</tr>
<tr>
<td>900-1100</td>
<td>concentration</td>
<td>Present results</td>
</tr>
</tbody>
</table>

#### Table

<table>
<thead>
<tr>
<th>Temperature Range (°C)</th>
<th>α₂</th>
<th>γ</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1169-1366</td>
<td>-</td>
<td></td>
<td>concentration</td>
<td>Kainuma, Inden (1997)</td>
</tr>
<tr>
<td>845-1310</td>
<td>10</td>
<td>312±6</td>
<td>concentration</td>
<td>Sprengel (1996)</td>
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<tr>
<td>881-1400</td>
<td>-</td>
<td>1.5</td>
<td>tracer</td>
<td>Kroll (1992)</td>
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<tr>
<td>897-995</td>
<td>0.3</td>
<td>290±15</td>
<td>tracer</td>
<td>Rüsing, Herzig (1995)</td>
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<tr>
<td>897-995</td>
<td>n/a</td>
<td>≈350</td>
<td>concentration</td>
<td>Rüsing, Herzig (1995)</td>
</tr>
<tr>
<td>750-1250</td>
<td>1.5x10⁻⁶</td>
<td>117±5</td>
<td>concentration</td>
<td>Hirano, Iijima (1984)</td>
</tr>
<tr>
<td>900-1100</td>
<td>0.3</td>
<td>290±25</td>
<td>concentration</td>
<td>Present results</td>
</tr>
</tbody>
</table>

#### Diagrams

- **α₂-Ti₃Al**: The Arrhenius plots show the relationship between $D_0$ and $10^4/T$ for different temperatures. The data points are plotted and fitted with lines to show the trend.
- **γ-TiAl**: Similar to α₂-Ti₃Al, the Arrhenius plots illustrate the relationship between $D_0$ and $10^4/T$ for γ-TiAl, with data points and fitted lines.

#### Equations

- $D_0 = \alpha^2 D_\gamma$ for α₂-Ti₃Al
- $D_\gamma = \gamma D_\alpha$ for γ-TiAl

#### Parameters

- $D_0$: Pre-exponential factor (cm²s⁻¹)
- $E_a$: Activation energy (kJmol⁻¹)
- $D_\alpha$: Diffusion coefficient for α₂-Ti₃Al
- $D_\gamma$: Diffusion coefficient for γ-TiAl
- $\alpha^2$: Coefficient for α₂-Ti₃Al
- $\gamma$: Coefficient for γ-TiAl
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

\[ \tilde{J}_O = -\frac{D^O_{oo}}{\partial x} + \frac{D^O_{OAl}}{\partial x} \leq 0 \]

- predict interdiffusion coefficient ratio:

\[ \frac{D^O_{OAl}}{D^O_{oo}} = -\frac{\Delta C_O}{\Delta C_{Al}} \]

$T = 1100^\circ C$

$\frac{D^O_{OAl}}{D^O_{oo}} = 0.44 \pm 0.08$
calculated $\tilde{D}_{oo}$

- $\tilde{J}_o^i = -\tilde{D}_{oo} \frac{\partial C_O}{\partial x} - \tilde{D}_{oo} \frac{\partial C_{Al}}{\partial x}$, no intersecting diffusion paths...
- region of pure O enrichment, $\frac{\partial C_{Al}}{\partial x} = 0 \implies \tilde{J}_o^i = -\tilde{D}_{oo} \frac{\partial C_O}{\partial x}$
- 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>$\tilde{D}_{oo}^{10}$ $(10^{-10} \text{cm}^2\text{s}^{-1})$</th>
<th>Arreheinus Behaviour</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$1100^\circ C$</td>
<td>1000$^\circ C$</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>

$\tilde{D}_{oo} / \tilde{D}_{Al} = 100 \sim 1000$
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
constant Ti / Al ratio

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

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

$\bar{J}_0 = -D_{oo}^{\text{Ti}} \frac{\partial C_0}{\partial x} - D_{oo}^{\text{Al}} \frac{\partial C_{\text{Al}}}{\partial x}$

$\rightarrow \bar{J}_0 = -D_{oo}^{\text{Ti}} \frac{\partial C_0}{\partial x}$

$x_m - x_o = 186 \mu m$

$x_m - x_o = 109 \mu m$

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

$J_0$ ($10^{-10}\text{mole/cm}^2\text{s}$) vs. $x$ ($\mu\text{m}$)

$D_0$ ($10^{-10}\text{cm}^2/\text{s}$) vs. $C_0$ (mole/cm$^3$)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$\tilde{D}_{oo}$ ($10^{-10}\text{cm}^2/\text{s}$) $T = 1100^\circ\text{C}$</th>
<th>Ti / Al (couple)</th>
<th>$\tilde{D}_{oo}$ ($10^{-10}\text{cm}^2/\text{s}$) $T = 1100^\circ\text{C}$</th>
<th>$\alpha_2$(O) / $\alpha_2$(O) couples</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>
<td></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>
<td></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>
<td></td>
</tr>
</tbody>
</table>

$\tilde{D}_{oo}$ ~ independent of $X_0$ 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: $\text{Ti-Al} \rightarrow O$
- $\text{Ti-Al}$ interaction zone decreases with $X_O$
  - $O \rightarrow \text{Ti-Al}$: kinetic / thermodynamic?
  - expect similar $\Delta \mu_{(\text{Ti,Al})}$ 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

“up-hill” Al diffusion

- 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 $a$(Al), decrease $a$(Ti) (or both)

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

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

multi-cell KEMS

pressure measurement

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

activity measurement

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

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

( \( i = Ti, Al, Al_2O \) )
\( a(\text{Al}) \) vs. \( X_O \)

![Graph showing the relationship between \( a(\text{Al}) \) and \( 10^4/T (\text{K}^{-1}) \) for different Ti-Al-O alloys at various temperatures. The graph includes data points and trend lines for each alloy, with labels for the phases \( \alpha_2(O) \), \( \gamma + \text{Al}_2\text{O}_3 \), and \( \alpha\text{-Ti(Al,O)} \). The reference state is \( \{\text{Al(l)} + \text{Al}_2\text{O}_3(\text{s})\} \).]
$a(\text{Ti})$ vs. $X_O$

$T(\degree C)$

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

Increasing O

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

$0.1$ $0.2$ $0.3$ $0.4$ $0.5$ $0.6$ $0.7$ $0.8$ $0.9$ $1$

$\alpha$-Ti(Al,O)

references state: $\{\text{Ti(s)} + Y_2O_3(s)\}$
• $\alpha_2 / Al_2O_3$ 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
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