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>
$\alpha_2$-Ti$_3$Al / Al$_2$O$_3$ couples

![Micrographs showing the growth of oxide scale on Ti-32Al / Al$_2$O$_3$ couples at 1100°C, 1000°C, and 900°C after 500 hours.](image)

**Graph:**
- Thickness vs. square root of time for each temperature.
- Data points and error bars for each temperature.

**Equations:**
- $k_p = 4.0 \pm 0.2$ at 1100°C
- $k_p = 0.72 \pm 0.04$ at 1000°C
- $k_p = 0.12 \pm 0.02$ at 900°C
\[ \alpha_2-\text{Ti}_3\text{Al} \ / \ \text{Al}_2\text{O}_3 \text{ couples} \]

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

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

\( \bar{J}_O \gg \bar{J}_{AI} \) (from diffusion path)

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

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

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

\[ \bar{J}_O \text{ from low to high } X_O: \quad \bar{J}_O = -\bar{D}^{\text{Ti}}_{OO} \frac{\partial C_O}{\partial x} - \bar{D}^{\text{Ti}}_{OAI} \frac{\partial C_{\text{Al}}}{\partial x} \]

\( \bar{D}_{OAI} \) must be +ve and significant...

+ve thermodynamic interaction between O and Ti + Al

\[ T = 1100^\circ\text{C} \]
treatment diffusion in Ti-Al-O

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

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

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

Al₂O₃ / Ti-25Al
T = 1100°C, 250 h

concentration profiles

raw EPMA data

EPMA error, TiO₂-layer

“up-hill” diffusion of O

Ti and Al aren’t diffusing!

corrected profile

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

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

![Graph showing interdiffusivity values for different alloys at various temperatures.]

### Table: Interdiffusivity Values

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$\tilde{D}_\gamma$ (cm$^2$sec$^{-1}$)</th>
<th>$\tilde{D}_\alpha$ (cm$^2$sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1100°C</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti-25Al</td>
<td>$9.9 \pm 0.5 \times 10^{-11}$</td>
<td>$2.7 \pm 0.3 \times 10^{-12}$</td>
</tr>
<tr>
<td>Ti-32Al</td>
<td>$6.3 \pm 0.6 \times 10^{-11}$</td>
<td>$3.0 \pm 1.5 \times 10^{-12}$</td>
</tr>
<tr>
<td>Ti-35Al</td>
<td>$5.4 \pm 0.3 \times 10^{-11}$</td>
<td>$5.2 \pm 1.3 \times 10^{-12}$</td>
</tr>
<tr>
<td>Ti-33.3Al-5O</td>
<td>$6.1 \pm 0.7 \times 10^{-11}$</td>
<td>$1.2 \pm 0.2 \times 10^{-12}$</td>
</tr>
<tr>
<td><strong>1000°C</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti-25Al</td>
<td>$2.8 \pm 0.4 \times 10^{-11}$</td>
<td>$2.6 \pm 0.5 \times 10^{-13}$</td>
</tr>
<tr>
<td>Ti-32Al</td>
<td>$5.9 \pm 0.9 \times 10^{-11}$</td>
<td>$3.3 \pm 0.7 \times 10^{-13}$</td>
</tr>
<tr>
<td><strong>900°C</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti-25Al</td>
<td>$5.1 \pm 2.0 \times 10^{-12}$</td>
<td>$3.4 \pm 0.9 \times 10^{-14}$</td>
</tr>
<tr>
<td>Ti-32Al</td>
<td>$1.4 \pm 0.5 \times 10^{-11}$</td>
<td>$3.9 \pm 1.0 \times 10^{-14}$</td>
</tr>
</tbody>
</table>

*average values*
Arrhenius behavior / comparison

<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></td>
<td>$D_0$ (cm$^2$s$^{-1}$)</td>
<td>$E_a$ (kJmol$^{-1}$)</td>
<td>$D_0$ (cm$^2$s$^{-1}$)</td>
<td>$E_a$ (kJmol$^{-1}$)</td>
</tr>
<tr>
<td>1169-1366</td>
<td>-</td>
<td>-</td>
<td>3.0x10$^{-3}$</td>
<td>210</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>-</td>
<td>1.5</td>
<td>291±10</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>≈350</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>750-1250</td>
<td>1.5x10$^{-6}$</td>
<td>117±5</td>
<td>2x10$^{-5}$</td>
<td>152±2</td>
</tr>
<tr>
<td>900-1100</td>
<td>0.3</td>
<td>290±25</td>
<td>1.1x10$^{-5}$</td>
<td>140±40</td>
</tr>
</tbody>
</table>
interstitial diffusion of O in \( \alpha_2\)-Ti₃Al

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

\[
\tilde{\mathcal{J}}_o = -\tilde{D}_{oo} \frac{\partial C_O}{\partial x} - \tilde{D}_{oal} \frac{\partial C_{Al}}{\partial x} \cong 0
\]

- predict interdiffusion coefficient ratio:

\[
\frac{\tilde{D}_{oal}}{\tilde{D}_{oo}} = -\frac{\Delta C_O}{\Delta C_{Al}}
\]

\[T = 1100^\circ C\]

\[\tilde{D}_{oal} \big/ \tilde{D}_{oo} = 0.44 \pm 0.08\]
calculated $\tilde{D}_{oo}$

- $\tilde{J}_0^i = -\tilde{D}_{oo} \frac{\partial C_o}{\partial x} - \tilde{D}_{oo} \frac{\partial C_{al}}{\partial x}$, no intersecting diffusion paths…
- region of pure O enrichment, $\frac{\partial C_{al}}{\partial x} = 0 \rightarrow \tilde{J}_0^i = -\tilde{D}_{oo} \frac{\partial C_o}{\partial x}$
- EPMA and micro-hardness; assume $\tilde{D}_{oo}$ const.

$$\frac{C(x, t) - C_s}{C_o - C_s} = \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right)$$

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$\tilde{D}_{oo}$</th>
<th>(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>
<td>900°C</td>
</tr>
<tr>
<td>I(Ti-25Al)</td>
<td>4.0±1.0</td>
<td>0.75±0.15</td>
<td>0.2±0.1</td>
</tr>
<tr>
<td>II(Ti-32Al)</td>
<td>5.5±1.5</td>
<td>0.6±0.15</td>
<td>0.15±0.1</td>
</tr>
<tr>
<td>III(Ti-35Al)</td>
<td>6.5±1.5</td>
<td>1.0±1.5</td>
<td>0.15±0.1</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 (1100ºC for 2 ~ 4 h); $T = 1100ºC$ for 100 h
- analysis: metallography, optical & EPMA
  - used multi-alloy EPMA standard... TiO$_2$ surface-layer
constant Ti / Al ratio

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

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

$x_{m} - x_{o} = 186\mu m$

$x_{m} - x_{o} = 109\mu m$

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

<table>
<thead>
<tr>
<th>alloy</th>
<th>$\tilde{D}_{OO}$ ($10^{-10}$ cm$^2$/s) $T = 1100$°C</th>
<th>Ti / Al (couple)</th>
<th>$\tilde{D}_{OO}$ ($10^{-10}$ cm$^2$/s) $T = 1100$°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>

$\tilde{D}_{OO}$ ~ independent of $X_O$ but small Ti / Al dependence (?)
$T = 1100^\circ C, 100 \text{ h}$

- Profiles flipped relative to diffusion path
- Classic “up-hill” profile for O...
  \[ \text{thermodynamic interaction: Ti-Al} \rightarrow \text{O} \]
- Ti-Al interaction zone decreases with $X_O$
  \[ \text{O} \rightarrow \text{Ti-Al: kinetic / thermodynamic ?} \]
- 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
- $X_0$ 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 → Ti-Al

- 9-1 diffusion path shows “up-hill” Al diffusion:
  - O dissolution must: increase \(a(\text{Al})\), decrease \(a(\text{Ti})\) (or both)
thermodynamic measurements

multi-cell KEMS

pressure measurement

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

activity measurement

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

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

(\( i = Ti, Al, Al_2O \))
$a(\text{Al})$ vs. $X_{\text{O}}$

$T(\degree \text{C})$

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

Increasing O

Reference state: $\{\text{Al(l) + Al}_2\text{O}_3(s)\}$
Reference state: \{ Ti(s) + Y_2O_3(s) \}

\[ I_{10/7}(K_T) \]

\[ \frac{1}{T(T)} \text{ vs. } X_0 \]

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

Temperature: 1400, 1300, 1200, 1100, 1000°C
summary

- $\alpha_2 / \text{Al}_2\text{O}_3$ and $\alpha_2(\text{O}) / \alpha_2(\text{O})$ couples... Ti-Al-O reaction behavior
- unsaturated $\alpha_2(\text{O})$ reduces $\text{Al}_2\text{O}_3$: $\gamma$-layer, “up-hill” $\tilde{J}_o$ in $\alpha_2(\text{O})$
- $\tilde{J}_o >> \tilde{J}_\text{Al}$; 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.”: $\tilde{D}_\text{OAl} / \tilde{D}_\text{OO}$ and $\tilde{D}_\text{OO}$, slight Ti / Al dependence
- $\alpha_2(\text{O}) / \alpha_2(\text{O})$ couples: confirm $\tilde{D}_\text{OAl} / \tilde{D}_\text{OO}$ and $\tilde{D}_\text{OO}$ 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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