Substitutional and Interstitial Diffusion in α₂-Ti₃Al(O)

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

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TMS Annual Meeting: 2/25 - 3/1/2007 – Orlando, FL, USA
\( \text{Ti-Al-O system} \)

\( T = 1000^\circ \text{C} \)

\( \text{Al}_2\text{O}_3 \) 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: $\alpha_2 / \text{Al}_2\text{O}_3$
  - 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 $T = 900, 1000, 1100^\circ$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>

no reaction, ignore

reaction, but ignore
**α₂-Ti₃Al / Al₂O₃ couples**

![Diagram of α₂-Ti₃Al / Al₂O₃ couples](image)

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

**Graph:**

- **ti-32Al / Al₂O₃,**
  - **t = 500 h**

**Thermal Stability:**

- 1100°C
- 1000°C
- 900°C

**Graph Details:**

- Thickness vs. sqrt. time (10⁻² s⁻¹)
- kₚ (10⁻¹⁵ cm²/s)
- kₚ = 4.0±0.2
- kₚ = 0.72±0.04
- kₚ = 0.12±0.02

**Marker:**

- Indicating the time period and material stability.
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 \( \gamma / \text{Al}_2\text{O}_3 \)

\( \vec{J}_O \gg \vec{J}_\text{Al} \) (from diffusion path)

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

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

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

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

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

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

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

+ve thermodynamic interaction between O and Ti + Al
treating 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”

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

concentration profiles

Al₂O₃ / Ti-25Al

T = 1100°C, 250 h

Ti and Al aren’t diffusing!

“up-hill” diffusion of O

raw EPMA data

EPMA error, TiO₂-layer

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

### Table

<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 \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>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>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

\( T = 1100^\circ C \)
Arrhenius behavior / comparison

### $\alpha_2$-Ti$_3$Al

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$D_0$ (cm$^2$s$^{-1}$)</th>
<th>$E_a$ (kJmol$^{-1}$)</th>
<th>$D_0$ (cm$^2$s$^{-1}$)</th>
<th>$E_a$ (kJmol$^{-1}$)</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1169-1366</td>
<td>-</td>
<td>-</td>
<td>3.0x10$^{-3}$</td>
<td>210</td>
<td>concentration</td>
<td>Kainuma, Inden (1997)</td>
</tr>
<tr>
<td>845-1310</td>
<td>10</td>
<td>312±6</td>
<td>2.8</td>
<td>295±10</td>
<td>concentration</td>
<td>Sprengel (1996)</td>
</tr>
<tr>
<td>881-1400</td>
<td>-</td>
<td>-</td>
<td>1.5</td>
<td>291±10</td>
<td>tracer</td>
<td>Kroll, (1992)</td>
</tr>
<tr>
<td>897-995</td>
<td>0.3</td>
<td>290±15</td>
<td>-</td>
<td>-</td>
<td>tracer</td>
<td>Rüsing, Herzig (1995)</td>
</tr>
<tr>
<td>897-995</td>
<td>n/a</td>
<td>≈350</td>
<td>-</td>
<td>-</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>2x10$^{-5}$</td>
<td>152±2</td>
<td>concentration</td>
<td>Hirano, Iijima (1984)</td>
</tr>
<tr>
<td>900-1100</td>
<td>0.3</td>
<td>290±25</td>
<td>1.1x10$^{-5}$</td>
<td>140±40</td>
<td>concentration</td>
<td>Present results</td>
</tr>
</tbody>
</table>

### $\gamma$-TiAl

- Kainuma
- Inden (1997)
- Sprengel (1996)
- Kroll (1992)
- Rüsing, Herzig (1995)
interstitial diffusion of O in \(\alpha_2\)-Ti\(_3\)Al

- \(\tilde{J}_0 >> \tilde{J}_{(Al,Ti)}\)… “transient equilibrium” (Kirkaldy et al. 1958-64)
O, local equilibrium; redistributes with Ti-Al substitutional lattice

\[
\tilde{J}_0 = -\tilde{D}_0 \frac{\partial C_O}{\partial x} - \tilde{D}_O \frac{\partial C_A}{\partial x} \approx 0
\]

- predict interdiffusion coefficient ratio:

\[
\frac{\tilde{D}_O}{\tilde{D}_0} = -\frac{\Delta C_O}{\Delta C_A}
\]

\(T = 1100^\circ C\)

\(\tilde{D}_O / \tilde{D}_0 = 0.44\pm0.08\)
calculated $\tilde{D}_{oo}$

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

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$\tilde{D}_{oo}^T$ ($10^{-10}$cm$^2$s$^{-1}$)</th>
<th>Arreheinious Behaviour</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1100°C 1000°C 900°C</td>
<td>$D_o$ (cm$^2$s$^{-1}$) $E_a$ (kJmole$^{-1}$)</td>
</tr>
<tr>
<td>I(Ti-25Al)</td>
<td>4.0±1.0 0.75±0.15 0.2±0.1</td>
<td>0.014 200±23</td>
</tr>
<tr>
<td>II(Ti-32Al)</td>
<td>5.5±1.5 0.6±0.15 0.15±0.1</td>
<td>0.60 240±37</td>
</tr>
<tr>
<td>III(Ti-35Al)</td>
<td>6.5±1.5 1.0±1.5 0.15±0.1</td>
<td>2.37 252±10</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 (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

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

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

\[ x_{\text{m}} - x_o = 186 \mu \text{m} \]

\[ x_{\text{m}} - x_o = 109 \mu \text{m} \]

\[ x_{\text{m}} - x_o = 173 \mu \text{m} \]
calculated $J_0$ and $\tilde{D}_{\text{OO}}$

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

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$\tilde{D}_{\text{OO}}$ ($10^{-10}$cm$^2$/s) $T = 1100^\circ$C</th>
<th>Ti / Al (couple)</th>
<th>$\tilde{D}_{\text{OO}}$ ($10^{-10}$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>
$T = 1100^\circ$C, 100 h

- profiles flipped relative to diffusion path
- classic “up-hill” profile for O...
  - thermodynamic interaction: Ti-Al → O
- Ti-Al interaction zone decreases with $X_O$
  - O → 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
- $X_{\text{O}}$ 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 → Ti-Al
- 9-1 diffusion path shows “up-hill” Al diffusion:
  - O dissolution must: increase $a$(Al), decrease $a$(Ti) (or both)
thermodynamic measurements

multi-cell KEMS

pressure measurement

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

activity measurement

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

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

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

$T(^{\circ}\text{C})$

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

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

$T(°C)$

$a(Ti)$

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

Increasing O

reference state: $\{Ti(s) + Y_2O_3(s)\}$
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” $\tilde{J}_0$ in $\alpha_2(\text{O})$
- $\tilde{J}_0 >> \tilde{J}_{\text{Al}}$: treat subst. and interstitial lattices independently
  - Ti-Al "pseudo binary" $\tilde{D} = \tilde{D}(C_i)$, scatter in data (effect of $X_0$)
  - "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 $X_0$ 0.005 → 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
acknowledgements:

Judy Auping (NASA Glenn), James Smith (NASA Glenn)
Christian Chatillon (Saint Martin d’Hères, France),
NASA Glenn Research Center – Directors Discretionary Fund
University of New South Wales, Sydney, Australia – ARC Grant