Combinatorial Assessment of the Oxidation Behavior of Titanium Alloys: Examples of Binary Ti-Mo, Ti-Cr, Ti-Al and Ti-W systems

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Outline

- Motivation and goals
- The LENS™
- Ti-xMo system
- Ti-xCr system
- Ti-xAl system
- Ti-xW system
Motivation and Goals

• There are numerous applications where the use of titanium alloys is desirable. However, their poor oxidation performance has limited their use in service → a need to increase the operating temperature

• The role of composition and microstructure on the evolution of the oxide layers, along with measurable properties (adherence, hardness, weight gain/loss) has not been well explored.

• Provide a generalized framework and critical information on operating oxidation mechanisms of Ti alloys in the composition and temperature space and develop a database of the synergistic effects of alloy content on the composition and structure of the oxide film.

• How does this translate to commercial alloys?

A series of compositionally graded binary systems
The LENS™ (Laser Engineered Net Shaping)

<table>
<thead>
<tr>
<th>Operating Parameters</th>
</tr>
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<tbody>
<tr>
<td>Powder Flow:</td>
</tr>
<tr>
<td>Laser Power:</td>
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<tr>
<td>Layer Thickness:</td>
</tr>
<tr>
<td>Hatch Width:</td>
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<tr>
<td>Travel Speed:</td>
</tr>
<tr>
<td>Energy Density:</td>
</tr>
</tbody>
</table>
Ti-xMo System
# Heat-treatment and Oxidation Test

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Solution Heat-treatment</th>
<th>Oxidation Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graded Ti-xMo</td>
<td>975°C for 3.5hr – water quenched</td>
<td>650°C for 25hr, 50hr and 100hr in still-air</td>
</tr>
</tbody>
</table>

Microstructures following solutionizing + WQ

![Image a](image_a.png)

![Image b](image_b.png)

![Image c](image_c.png)
Oxidation Tests (general observations)

Oxidation Tests at 650°C for 25hr

- Microstructure of the regions adjacent to the surface experience a drastic change
- Above 7.5 wt% Mo a eutectoid type microstructure forms near the surface which can extend up to 20 mm into the bulk.
Precipitation of $\beta$ from $\alpha$ (inverse phase transformation)

**Ti-3Mo**

- Intrагranular $\beta$ form where the content of oxygen in the alloy exceed a certain level
- Formation of these particles is highly sensitive to the content of O that causes a gradient of $\beta$ precipitates in a single lath

**Ti-6Mo**
Mechanism of inverse phase transformation

- O enrichment at the α interfaces
- Mo solubility in α and β is Highly sensitive to the O level
- Oxygen-assisted precipitation of β in α
**Ti-9Mo - Lamellar microstructure near the surface**

650°C - 25h

(Result of cooperative growth)

Lamellar microstructure near the surface

Oxide

Substrate

200 nm

1 μm
Ti-9Mo _ Evolution of Discontinuous Precipitation

\[ \beta \xrightarrow{\text{upon quenching}} \beta + \omega \xrightarrow{\text{at } 650^\circ C} \beta + \alpha \rightarrow \beta + \alpha \ ? \]

- Typical eutectoid phase transformations do not apply (monotectoid system)

Discontinuous precipitation

Previous microstructure (\( \alpha + \beta \)) is consumed by the new microstructure (\( \alpha + \beta \))
Example of Commercial Alloys

Ti64 with B
Oxidized at 950°C for 50hr

Ti64 with B
Oxidized at 820°C for 50hr

Ti64
Oxidized at 820°C for 50hr
Nano Indentation Results

Addition of Mo reduces the solubility of O in Ti -> Retards the starting point of linear oxidation and heavy oxide formation
Summary

• Precipitation of $\beta$ particles in $\alpha$ for compositions below $\sim$7.5%Mo as a result of O ingress

• Above $\sim$7.5 wt% Mo in the regions just below the surface and at the grain boundaries of prior $\beta$, discontinuous precipitation of $\alpha$ and $\beta$ phase takes place

• Scaling rate is unresponsive to the compositional variation in the composition-time space and a parabolic oxidation is being followed.
Ti-xCr System
Heat-treatment and Oxidation Tests

<table>
<thead>
<tr>
<th>Solution Heat-treatment</th>
<th>Oxidation Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>975°C for 35min – water quenched</td>
<td>650°C for 25hr, 50hr and 100hr in still-air</td>
</tr>
</tbody>
</table>

Examples of microstructure for Ti-xCr gradient following solutionizing + WQ

(a) Ti-3Cr
(b) Ti-9Cr
(c) Ti-17Cr
(d) Ti-30Cr
Formation of TiCr$_2$ in a narrow band adjacent to the surface (which is not expected below 5% Cr)

The narrow band extends slightly into the bulk and TiCr$_2$ particles also form at the grain boundaries

Uniform precipitation of TiCr$_2$ phase throughout the microstructure

- Oxygen ingress affects precipitation of TiCr$_2$
- Longer exposure time assist such a sluggish decomposition
No major change was observed in the microstructure with increase in holding time.

The β islands exist for 25 and 50 h, decompose after 100 h.
Thickness of the Oxide Layer

- At 20% Cr the plots level off
- Scale thickness is very sensitive to the Cr content and oxidation time
- Cr addition below a critical level degrades oxidation performance

**Burn resistant**
- C (Ti-35V-15Cr)
- BurTi (Ti-25V-15Cr-2Al-0.2C)
- Ti40 (Ti-25V-15Cr-xSi)
Oxide structure and composition

Ti-11Cr _ 25hr

[001] zone axis to ring pattern

L3
L2
L1

Pt

Metal

10μm
2μm

Intensity [arb. units]

2θ

20 30 40 50 60 70 80 90

(110) (101) (200) (111) (211) (220) (310) (311) (221) (202) (321)

TiO₂

rutil[001]
**Breakaway oxidation mechanism**

**Ti-11Cr 25hr**

![Image of Ti-11Cr precipitates]

**Nonstoichiometric Ti$_{1-x}$Cr$_x$ precipitates**

\[
\text{TiCr}_2 \rightarrow 2\text{Cr}^{3+}_{\text{Ti}} + V^0_{o} + \text{Ti}^{4+}_{\text{Ti}} \quad \text{Substitutional}
\]

\[
\text{TiCr}_2 \rightarrow 2\text{Cr}^{3+}_{\text{i}} + 6e^- + \text{Ti}^{4+}_{\text{Ti}} \quad \text{Interstitial}
\]

Cr carry effective negative charge if dissolved in TiO2 in interstitially -> increase in O vacancy for charge neutrality propose -> facilitates flux of O through the scale
Summary

- Close to the surface O enrichment alter the kinetics of TiCr₂ formation
- Above 20wt%Cr oxidation resistance is significantly increased
- The Laves phase particles do not immediately transform as the oxidation front passes, rather dissolve gradually and cause rapid oxidation after long enough time
Ti-xAl System
Oxidation test

- $\alpha$ and Ti$_3$Al are the expected phases across the composition range
- Dissimilar response to the polishing process -> Presence of Ti$_3$Al
Subsurface structure

transformation for the entire range of composition is attainable depending upon the level of oxygen ingress

Formation of Ti3Al which is avoided in γ Ti alloys, is beneficial here
Mixed oxide layer

Complex multilayer oxide:

- Similar thermodynamic stability of Ti and Al oxides
- Progressive alteration of balance in ionic transportation
- Stabilization of intermetallic phases in the substrate -> deviation from ideal Raultian behavior (linear relation between chemistry and the activity)


Schematic representation of oxide scales and oxygen diffusion zones

Formation of a protective alumina layer is not expected across this composition range
Scale thickness : $f (W \text{ wt\%}, \text{time})$

- for longer exposure times effect of composition is revealed
- Parabolic oxidation rate law
- Poor adhesion (spalled off locally)
- Higher Al concentration and other alloying elements are required for better performance
Summary

• Under certain oxidation condition and composition, Al₂O₃ can be found in the outermost layer

• Ingress of O induces a-\(\rightarrow\) Ti₃Al phase transformation at the surface

• Complexity of Ti-Al system is due to:
  
  o Similar thermodynamic stability of Ti and Al oxides
  
  o Progressive alteration of balance in ionic transportation direction
  
  o Stabilization of intermetallic phases in the substrate

• Parabolic oxidation rate law in the T-\(t\) domain

• Poor scale adhesion (higher Al concentration and other alloying elements are required)
Ti-x\text{W} System
Solutionizing + WQ

<table>
<thead>
<tr>
<th>Solution Heat treatment</th>
<th>Oxidation Test</th>
</tr>
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<tbody>
<tr>
<td>975°C for 100hr (in Ar)</td>
<td>650°C for 25hr, 50hr and 100hr</td>
</tr>
</tbody>
</table>

(a) Ti-2W  (b) Ti-7W  (c) Ti-12W  (d) Ti-17W  (e) Ti-22W  (f) Ti-25W

50μm

**Ti-(0-33)W**

<table>
<thead>
<tr>
<th>W (wt%)</th>
<th>α/α’</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>ω start</td>
<td>20 - 23.7</td>
<td></td>
</tr>
<tr>
<td>100% β</td>
<td>25 - 22.4 - 30</td>
<td></td>
</tr>
</tbody>
</table>

100hr at 650°C

- Similar morphology with size variation
- β phase in form of inter-lath and intra-lath particles
- (Not limited to the subsurface)
- for above Ti-23W Widmanstätten a/b
Lamellar structure

Ti-22W _ 25hr

- Form and develop at the partially reacted W particles
- Unlike the Ti-Mo not only in the regions with high concentration of O
**Scale thickness :** \( f(W \text{ wt%}, \text{ time}) \)

- The same trend for the all three (50nm<<1.5mm)

- Same thickness of a specific composition -> parabolic stage (associated with the diffusion of oxygen in the substrate)
Ti-12W _ 100 h

- compact outer layer (first formed) _ porous inner layer _ Extensive β precipitation

Distinct β particles at some of the lath boundaries are connected and created so called β ribs

Extremely fine β (less than few nm)
Internal oxidation where scaling rate is significantly lowered by high W addition!

Maybe attributed to the role of W stabilized β phase.
Summary

(1) Different morphologies including: α lath and β rib/precipitates (inter- and intra-lath), lamellar structure, Widmanstätten morphology

(2) The scale thickness decreases with addition of W and is unresponsive to the oxidation times range between 25-100hr.

(3) Ingress of oxygen leads to the extreme refinement of the microstructure just below the surface.

(4) Unexpected internal oxidation in Ti-25W with the Widmanstätten morphology.
Thank you