Oxidation of Alumina-Forming MAX Phases in Turbine Environments

James Smialek, Anita Garg, Bryan Harder, James Nesbitt, Timothy Gabb, Simon Gray*

NASA Glenn Research Center, Cleveland, OH
*Cranfield University, Cranfield, UK

Materials for High Temperature Applications: Next Generation Superalloys and Beyond
TMS Annual Mtg., San Diego, CA, Feb 26 - Mar 2
**Strain Tolerance:**

**Kinking and Crack Deflection in Cr$_2$Al(Si)C**

Bend test fracture; basal plane nano-laminate

$K_{IC} = 6.6 \text{ MPa}/\mu\text{m}^{1/2}$

(0001) Sliding

$(\text{Cr-Al})/(\text{Cr-C})=0.40 \sigma_{\text{bond}}, 0.43 \gamma_{\text{cleav}}.$

W. Yu, S. Li, W.G. Sloof, 2007

Lin et al. 2006
Commercial Ti$_2$AlC 211 MAXthal (Sandvik/Kanthal)
M. Sundberg, G. Malmqvist, A. Magnusson, T. El-Raghy, 2004

8000 cycles to 1350°C!

15 μm Al$_2$O$_3$
Cr₂AlC

Li, 2014

Bend Strength
after Water Quench

1 cycle
5 cycles

from 1325°C

700 MPa Compressive strength retained (Gleeble test) after -90°C/s quench from 1200°C

Ti₂AlC

Adamaki, 2016

Thermal Shock of M₂AlC
(thermal conductivity x strength) / (CTE x modulus)
Some ~50 MPa Ti$_3$SiC$_2$ High Temperature Bend Strength
(Sun, 2006)
Motivation and Rationale

**Ti\textsubscript{3}AlC\textsubscript{2}, Ti\textsubscript{2}AlC, Cr\textsubscript{2}AlC**

- $\alpha$-Al\textsubscript{2}O\textsubscript{3} formers, (slow, low-volatility)
- Na\textsubscript{2}SO\textsubscript{4} corrosion resistance
- CTE close to YSZ, $\alpha$-Al\textsubscript{2}O\textsubscript{3}
- Damage (Strain ?) tolerance,
  - nano-laminate shear, machinable
- Thermal shock resistance: $\sim$1400°C quench
- $K_{IC} \approx 7$ MPa·m\textsuperscript{1/2}
Kanthal Ti$_2$AlC, Cr$_2$AlC

1. High temperature $\alpha$-Al$_2$O$_3$ kinetics
2. High pressure burner rig
3. YSZ Thermal Barrier Coatings
4. Superalloy/MAX Phase Hybrids
5. Hot corrosion/LCF
1) High temperature $\alpha$-Al$_2$O$_3$ kinetics

- Al$_2$O$_3$ grain boundary diffusivity
- transient TiO$_2$ growth
- cubic kinetics

“Oxygen Permeability and Grain-Boundary Diffusion Applied to Alumina Scales,”

NASA TM 217855, pp. 1–14, August 2013.
1300°C Ti$_2$AlC TGA:
Rapid TiO$_2$ Transients on heating

TGA Oxidation of Ti$_2$AlC in Air

![Graph showing corrected mass gain vs. corrected time for Ti$_2$AlC oxidation in air. The graph includes multiple lines representing different temperatures, with a trend line indicating a $1/3$ power relationship. The graph also highlights the oxidation time of Tallman 1200 as approximately 3000 hours.]
Arrhenius Plot of Cubic Oxidation Rate for Ti<sub>2</sub>AlC

- Temperature points: 1400°C, 1300°C, 1200°C, 1100°C, 1000°C
- Rate constant formula: $A = 2.485 \times 10^{10}$
- Activation energy: $Q = 334$ kJ/mol
- Coefficient of determination: $r^2 = 0.998$
Scale Grain Boundary Diffusivity
MAX Compounds and FeCrAl(X) Alloys

\[ \Pi_i = k_{p,i} \cdot G_i \approx 12 \delta D_{gb,O,interface} \]

\[ Q_{gb,O} = 375 \pm 25 \text{ kJ/mole} \]

“Oxygen diffusivity in alumina scales grown on Al-MAX phases,”
2) First high pressure burner rig test of Ti$_2$AlC

(1100°-1300°C, Jet A fuel, 25 m/s, 6 atm., 10% water vapor)

- transient TiO$_2$ growth
- cubic kinetics
- H$_2$O - scale volatility issues (?)

High Pressure Burner Rig
H₂O ≈ 10%

Sample holder

Up to ~1500°C, ~15 atm, ~200 m/s
(decommissioned 2016)
HPBR SiC/SiC CMC *Paralinear* Weight Change

(1100 °C-1300°C, 6 atm, 25 m/s; Robinson/Smialek 1998)

\[
\{ \text{SiC} + \text{H}_2\text{O}/\text{O}_2 \} \rightarrow \text{SiO}_2 (s) \rightarrow \text{Si(OH)}_4 (g)
\]

(Opila et al., 1998-2006)
HPBR Oxidation \textit{Gains} for Ti$_2$AlC

(6 atm, 25 m/s)

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Mass Gain, mg/cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1300°C</td>
<td></td>
</tr>
<tr>
<td>1200°C</td>
<td></td>
</tr>
<tr>
<td>1100°C</td>
<td></td>
</tr>
</tbody>
</table>

\textbf{TiO$_2$} 2 h

\textbf{Al$_2$O$_3$} 1300°C
Offset Corrected Ti$_2$AlC HPBR Oxidation:

Good cubic behavior, $\sim$1/2 TGA

\[ \Delta W/A = (kt)^{1/n} \]

\[ 1/n = 0.30 - 0.33 \]

\[ r^2 = 0.98 - 0.99 \]
HPBR after 1300°C Pre-oxidation of Ti$_2$AlC

(6 atm, 25 m/s)

mass gain, mg/cm$^2$

Subsequent HPBR loss rate

ΔW

HPBR
HPBR Recession Rates for Ti$_2$AlC and SiC

6 atm., 25 m/s

mass loss rate, mg/cm$^2$/h

$1/T$, $10^4$/K

0.1

SiC

pre-oxidized Ti$_2$AlC

SiC

Regression

0.01

~5x

Ti$_2$AlC:

0.017 mg/cm$^2$/h

1400
1300
1200°C

$1/T$, $10^4$/K

0.01
$\text{TiO}_2$ Reduced in 1200°C HPBR Exposures

HPBR, 50 h

TGA, 100 h

44% TiO$_2$

1.6% TiO$_2$
## Hybrid Concepts (EBC/TBC) Enabled by MAX Phases

Intermediate CTE, Strain Tolerance, YSZ Compatibility
Liner, Seals, Bond Coats (?)

### CTE (10^{-6}/°C)

<table>
<thead>
<tr>
<th>Material</th>
<th>CTE (10^{-6}/°C)</th>
<th>Layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSZ</td>
<td>10</td>
<td>Top Coat</td>
</tr>
<tr>
<td>( \text{Al}_2\text{O}_3 )</td>
<td>9</td>
<td>Scale</td>
</tr>
<tr>
<td>( \text{Ti}_2\text{AlC} )\n</td>
<td>( \text{Ti}_3\text{AlC}_2 )</td>
<td>8 9</td>
</tr>
<tr>
<td>Rene N5</td>
<td>15</td>
<td>Substrates</td>
</tr>
<tr>
<td>SiC CMC</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Mo, Nb, Ti</td>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>

Critical interface
Attachment ?
3) YSZ Thermal Barrier Coatings on MAX Phases

- APS and PS-PVD (~100 µm)
- Ti₂AlC (CTE 9); Cr₂AlC (CTE 13)
- Stepped furnace test
  - 1100° - 1300° C
  - 500 h each → 2500 h

“Oxidative Durability of TBCs on MAX Phase Substrates,”
Plasma Spray-Physical Vapor Deposition
PS-PVD

...2 m long, 1 m diameter...
plasma core over 6,000°C; 2000 m/s....
Interrupted Oxidation of PS-PVD YSZ on Ti$_2$AlC

The graph shows the mass gain (mg/cm$^2$) vs. time (hours) for different temperatures: 1000°C, 1100°C, 1150°C, 1200°C, 1250°C, and 1300°C. Each temperature has a corresponding oxide thickness: 6 µm, 11 µm, 16 µm, 24 µm, and 35 µm. The data points are represented by different symbols for each temperature, with Al$_2$O$_3$ shown at 35 µm.
Intact PS-PVD TBC
(Ti$_2$AlC, 1300°C, 500 h) SEM/BSE

Ni plate

7 YSZ, 70 µm

Al$_2$O$_3$, 36 µm

Ti$_2$AlC

Q267AuPd 15.0kV 11.9mm x500 GWBSE
TBC FCT Life Comparison to Literature: “The 7 µm Rule”

Alumina Scale Thickness at TBC Failure

EB-PVD TBC FCT Life on Alumina-Forming Systems

- Ti$_2$AlC: 35 µm, PS-PVD
- Pt-Al TGA: 7 µm Al$_2$O$_3$

- 650 h (-3700 MPa)
- 20,000 h (680 MPa)

@1150°C
Hybrid Concepts with MAX Phases
Intermediate CTE, Strain Tolerance, 
LTHC Corrosion Resistance

<table>
<thead>
<tr>
<th>CTE, $10^{-6}/^\circ$C</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Na$_2$SO$_4$</strong></td>
</tr>
<tr>
<td>Al(Cr)$_2$O$_3$</td>
</tr>
<tr>
<td>Cr$_2$AlC</td>
</tr>
<tr>
<td>Superalloy</td>
</tr>
</tbody>
</table>

Interface stability
4) \( \text{Cr}_2\text{AlC} / \text{Ni-base Superalloys Interfacial Stability:} \)

LTHC Corrosion resistant coating? (92% LCF deficit)

1100°C hot pressed diffusion couples

- 0.3 - 3 mm, 2 h @ 10^{-6} \text{ torr}
- \text{Cr}_2\text{AlC} on LSHR disk alloy (or Rene’N5)

800°C (or 1150°C) diffusion/oxidation

- 100 h, 1000 h

“Interfacial Reactions of a MAX Phase-Superalloy Hybrid”
*Surface and Interface Analysis, 276 (2015) 31*
Survives 1000 h of 800°C Furnace Oxidation
LSHR - Cr$_2$AlC DC3 Hybrid Couple

- LSHR
- Cr$_2$AlC
- Hybrid couple

mass gain, mg/cm$^2$

mass gain vs. time, hours

Inset image showing LSHR and Cr$_2$AlC layers with noted thicknesses of 1.8 mm and 1.2 mm.
As-Hot Pressed Cross Section
(2h @ 1100°C produced ~ 50 µm layer)

LSHR

NiAl + Cr₇C₃ Diffusion Zone 45 µm

260 µm MAX layer

SEM/BSE
Minor Diffusion Zone Growth at 800°C
LSHR Alloy/Cr$_2$AlC

- Total DZ
- Cr$_7$C$_3$ band
- β-Ni(Co)Al inner layers

1100°C, 4 h Hot press

<table>
<thead>
<tr>
<th>Time, hours</th>
<th>Diffusion Zone, µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5 µm</td>
</tr>
<tr>
<td>200</td>
<td></td>
</tr>
<tr>
<td>400</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td></td>
</tr>
<tr>
<td>800</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td></td>
</tr>
</tbody>
</table>
Cr$_2$AlC-Rene'N5 Hybrid Couple: Interdiffusion at 1150°C

 Plot showing interdiffusion at 1150°C with interface width in µm on the y-axis and time in hours on the x-axis. The graph shows a linear increase in interface width with time, indicating interdiffusion. The failure point is marked on the graph.
DC4: Cr$_2$AlC/Rene’N5

As Hot-Pressed
1100°C, 2 h

Rene’N5

Cr$_2$AlC

Oxidized
1150°C, 100 h

Rene’N5

Cr$_2$AlC

200 µm
III) Reaction Zone

IV) Depletion Zone

Cr$_7$C$_3$

Al$_2$O$_3$

NiAl

Cr$_2$AlC

Cracks

DC4: Cr$_2$AlC/N5 (1150°C, 100 h) 200-250 x
Hybrid Concepts with MAX Phases
Intermediate CTE, Strain Tolerance, LTHC Corrosion Resistance

CTE, $10^{-6}/^{\circ}C$

<table>
<thead>
<tr>
<th></th>
<th>Salt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$SO$_4$</td>
<td></td>
</tr>
<tr>
<td>Al(Cr)$_2$O$_3$</td>
<td>9</td>
</tr>
<tr>
<td>Cr$_2$AlC</td>
<td>13</td>
</tr>
<tr>
<td>Superalloy</td>
<td>15</td>
</tr>
</tbody>
</table>

Critical chemistry

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5) Cr$_2$AlC / Disk Alloy Hot Corrosion:

700°C **bulk** LTHC:
500 h, (Na,K)$_2$SO$_4$ (T$_e$ = 823°C)

760°C **Coated** LSHR LCF:
840 / -430 MPa at 0.33Hz
50 h, (Na,Mg)$_2$SO$_4$ (T$_e$ = 660°C)
Type II LTHC of Cr$_2$AlC (3) and Superalloys (7)  
700°C, 500 h, 0.5 mg/cm$^2$ salt recoat every 50 h

300 ppm SO$_2$  
80Na$_2$SO$_4$–20K$_2$SO$_4$ salt (823°C)

Dr. Simon Gray  
Cranfield University
500hrs, surface macros

\( \text{Cr}_2\text{AlC} \)

\( \text{LSHR} \)

\( \text{N5} \)
Sulfur maps

Cr$_2$AlC LSHR

Al, Ni, Co

Na, S, Cr

Dr. Simon Gray
Cr$_2$AlC Max Phase Coatings on LSHR
Prevents LTHC Pitting, LCF Debit

(Na,Mg)SO$_4$ paste; in air

**LCF Life**

<table>
<thead>
<tr>
<th>Test Condition</th>
<th>LCF Life (thousands of cycles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Exposure</td>
<td>Uncoated 120</td>
</tr>
<tr>
<td>Cr$_2$AlC</td>
<td>Uncoated 40</td>
</tr>
<tr>
<td>Cr$_2$AlC</td>
<td>0</td>
</tr>
<tr>
<td>Oxidation (500h, 760°C)</td>
<td>Uncoated 80</td>
</tr>
<tr>
<td>Cr$_2$AlC</td>
<td>0</td>
</tr>
<tr>
<td>Hot Corrosion (50h, 760°C)</td>
<td>Uncoated 12</td>
</tr>
<tr>
<td>Cr$_2$AlC</td>
<td>-92%</td>
</tr>
</tbody>
</table>
Cr$_2$AlC Corrosion Resistance on LSHR Disk Alloy (LCF Samples)

As-processed heat treated 760°C, 8 h

+760°C, 500 h oxidation + 50 h hot corrosion
Ti$_2$AlC, Cr$_2$AlC MAX Phases: Items of Potential Interest for Turbines

1. Rate Control by Al$_2$O$_3$ grain boundary diffusion; cubic rate protective to 1400°C; Q = 334 kJ/mole
2. Ti$_2$AlC stable in 1300°C combustion (HPBR) gas.
3. Extensive TBC furnace life @ 1300°C for Ti$_2$AlC.
4. Superalloy / Cr$_2$AlC hybrids stable: 800°C, but not 1150°C.
5. Minimal 700°C Type II LTHC of Cr$_2$AlC

INTRIGUING ALUMINA FORMERS
1. Ti$_2$AlC breakaway TiO$_2$ growth:
   < critical Al content; or damaged areas
2. Cr$_2$AlC isothermal oxidation: CrO$_3$ losses (Cr$_7$C$_3$)
3. Cr$_2$AlC cyclic oxidation:
   interfacial spallation; Cr$_7$C$_3$ depletion zones
4. Superalloy / Cr$_2$AlC compatibility:
   interdiffusion at, delamination from 1150°C.
<table>
<thead>
<tr>
<th>substrate</th>
<th>MAX phase</th>
<th>top coat</th>
<th>use</th>
<th>advantage</th>
<th>max temp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>Ti$_2$AlC</td>
<td>none</td>
<td>gas path</td>
<td>protective $k_c$, low volatility, adherent Al$_2$O$_3$</td>
<td>~1300°C</td>
</tr>
<tr>
<td>none</td>
<td>Ti$_2$AlC</td>
<td>YSZ</td>
<td>TBC</td>
<td>CTE match, adherent Al$_2$O$_3$</td>
<td>~1300°C</td>
</tr>
<tr>
<td>superalloy</td>
<td>Cr$_2$AlC</td>
<td>none</td>
<td>hot corrosion</td>
<td>higher CTE, Cr, Al</td>
<td>~900°C</td>
</tr>
</tbody>
</table>