Sulfur and Moisture Effects on Alumina Scale and TBC Spallation

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It has been well established that a few ppmw sulfur impurity may segregate to the interface of thermally grown alumina scales and the underlying substrate, resulting in bond degradation and premature spallation. This has been shown for NiAl and NiCrAl-based alloys, bare single crystal superalloys, or coated superalloys. The role of reactive elements (especially Y) has been to getter the sulfur in the bulk and preclude interfacial segregation. Pt additions are also very beneficial, however a similar thermodynamic explanation does not apply.

The purpose of the present discussion is to highlight some observations of these effects on Rene’142, Rene’N5, PWA1480, and PWA1484. For PWA1480, we have mapped cyclic oxidation and spallation in terms of potential sulfur interfacial layers and found that a cumulative amount of about one monolayer is sufficient to degrade long term adhesion. Depending on substrate thickness, optimum performance occurs if sulfur is reduced below about 0.2-0.5 ppmw. This is accomplished in the laboratory by hydrogen annealing or commercially by melt-fluxing.

Excellent 1150°C cyclic oxidation is thus demonstrated for desulfurized Rene’142, Rene’N5, and PWA1484. Alternatively, a series of N5 alloys provided by GE-AE have shown that as little as 15 ppmw of Y dopant was effective in providing remarkable scale adhesion. In support of a Y-S gettering mechanism, hydrogen annealing was unable to desulfurize these alloys from their initial level of 5 ppmw S. This impurity and critical doping level corresponds closely to YS or Y2S3 stoichiometry.

In many cases, Y-doped alloys or alloys with marginal sulfur levels exhibit an oxidative sensitivity to the ambient humidity called Moisture-Induced Delayed Spallation (MIDS). After substantial scale growth, coupled with damage from repeated cycling, cold samples may spall after a period of time, breathing on them, or immersing them in water. While stress corrosion arguments may apply, we propose that the underlying cause is related to a hydrogen embrittlement reaction: Al_{alloy} + 3 H_2O = Al(OH)_3 + 3H^+ + 3e^- . This mechanism is derived from an analogous moisture-induced hydrogen embrittlement mechanism originally shown for Ni3Al and FeAl intermetallics. Consequently, a cathodic hydrogen charging technique was used to demonstrate that electrolytic de-scaling occurs for these otherwise adherent alumina scales formed on Y-doped Rene’N5, in support of hydrogen effects.

Finally, some TBC observations are discussed in light of all of the above. Plasma sprayed 8YSZ coatings, produced on PWA1484 without a bond coat, were found to survive more than 1000 1-hr cycles at 1100°C when desulfurized to below 0.1 ppmw. At higher sulfur (1.2 ppmw) levels, moisture sensitivity and delayed TBC failure, referred to as Desk Top Spallation, occurred at just 200 hr. Despite a large degree of scatter, a factor of 5 in life improvement is indicated for desulfurized samples in cyclic furnace tests, confirming the beneficial effect of low sulfur alloys on model TBC systems. (DTS and moisture effects are also observed on commercially applied PVD 7YSZ coatings on Rene’N5+Y with Pt-aluminide bond coats). These types of catastrophic failure were subverted on the model system by segmenting the substrate into a network of 0.010” high ribs, spaced ¼ in. apart, prior to plasma spraying. No failures occurred after 1000 cycles at 1150°C or after 2000 cycles at 1100°C, even after water immersion. The benefit is described in terms of elasticity models and a critical buckling stress.
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May 9, 2007, Evendale, OH
Outline of Review

• Overview of compositional effects
• Critical sulfur content and Y/S ratio
• Moisture-induced delayed spallation;
• Desk Top Spallation
• Cyclic models (COSP for Windows)
## Compositions and Prevalent Scale Components

(Weight %)

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<tr>
<th>alloy</th>
<th>Co</th>
<th>Al</th>
<th>Cr</th>
<th>Ta</th>
<th>W</th>
<th>Mo</th>
<th>Re</th>
<th>Ti</th>
<th>Hf</th>
<th>S ppmw</th>
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<td>0</td>
<td>0.2</td>
<td>3-6</td>
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Al₂O₃, Ni(Al,Cr)₂O₄, CrTaO₄, NiTa₂O₆, HfO₂, Cr₂O₃, NiO, TiO₂

(protective, neutral, detrimental)
Oxidation Issues for Ni-base Superalloys

- \( \text{Al}_2\text{O}_3 \) protective scales; external vs internal oxidation
- \( \text{NiAl}_2\text{O}_4, \text{NiTa}_2\text{O}_6, \text{CrTaO}_4 \) relatively innocuous
- Layered:
  - a) \( \text{NiAl}_2\text{O}_4, \text{NiTa}_2\text{O}_6 \) outer transients
  - b) \( \text{Al}_2\text{O}_3 \) inner layer
- \( \text{Cr}_2\text{O}_3 (?) \), \( \text{NiCr}_2\text{O}_4, \text{NiO, TiO}_2, \text{HfO}_2 \) non-protective scale
- \( \text{NiMoO}_4, \text{NiWO}_4, \text{CrNbO}_4, \text{V}_2\text{O}_5 \), etc. also detrimental
- Co generally acts in concert with Ni
- S (adhesion) control:
  - a) Y (Hf, Zr?) and gettering
  - b) or desulfurization
Transient Scale and Alumina
High S 1484, 1200°C, 25 h Air/75 h Ar
# Ranking Diagram of 25 Ni Superalloys

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<tr>
<th>Alloy</th>
<th>$\Delta W/A$</th>
<th>Al</th>
<th>Cr</th>
<th>Ti</th>
<th>Ta</th>
<th>Nb</th>
<th>Mo</th>
<th>W</th>
<th>ratio</th>
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**1100°C, 200 hr mg/cm²**

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<tr>
<th></th>
<th>avg=</th>
<th>stdev=</th>
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<td></td>
<td>7.04</td>
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Inverse Correlation of Aluminum and Chromium in 25 Superalloys

$\text{Al} + 0.22 \text{ Cr} = 7.25$

$r^2 = 0.70$

conventional SA
fitted line
Predicted Cyclic Oxidation Weight Change
Ni-(6Co-6Al-6Cr-6Ta)-(1Ti-1Nb-1Mo-1W)-(0.2Hf-0.1C)
Diffusion Controlled Desulfurization

$H_2$ \rightarrow \text{oxide-free surface} \rightarrow S \rightarrow H_2S$ ?

$C_S \sim \frac{D_S t}{L^2}$

S diffusion

superalloy coupon
Effect of Sulfur Content on the 1100°C Cyclic Oxidation of PWA 1480
Oxide Adherence Map for Desulfurized PWA1480
1100 C, 1-hr Cycles, 500 Hours

Sulfur content, C_s, ppmw

Sample thickness, mm

mg/cm²
< -30
-20/-30
-10/-20
-5/-10
-1/-5
+1/-1

Non-adherent
10 Monolayers
10 mg/cm²
0 mg/cm²
1 Monolayer
Adherent
• **PWA 1480**

  – Distinct *critical sulfur content* and thickness effect

  – \( \approx 0.2 \text{ ppmw } S @ 1 \text{ mm (40 mils)} \)

  – \( \approx 1 \text{ monolayer} \) total segregation (cf. 0.5 at saturation)
Improved 1100°C Cyclic Oxidation
PWA 1480 to 1484

1480, (ca. 1988) 6.7 ppmw S
1480, H₂, 1200°C / 100 hr, 0.2 ppmw S
1484, (ca. 1998), 1.2 ppmw S
1484, H₂, 1250°C / 50 hr, 0.01 ppmw S

1480, 6.7 S (1.5 Ti)
1484, 1.2 S
1480, 0.2 S
1484, 0.01 S

1-hr cycles
Improved 1000°C Cyclic Oxidation
Rene’ N4 to N5±Y, N6

-10
-8
-6
-4
-2
0
2

1-hr cycles

Rene’ N4
Rene’ N5-
Rene’ N5+
Rene’ N6
(4Al 4Ti)
(6Al)

N5,6

National Aeronautics and Space Administration
www.nasa.gov
Exceptional $1150^\circ C$ Cyclic Oxidation:

PWA 1484 and Rene’N5

- Rene’N5 - (ca. 1992)
- Rene’N5 -, $H_2$-annealed, $1200^\circ C / 100$ hr
- PWA1484, PCC melt desulfurized, (ca. 1998) 0.3 ppmw $S$

1484 melt deS
0.3 $S$

N5-, $H_2$
$\sim0.3$ $S$

N5- 
$\sim3$ $S$
1100°C Cyclic Oxidation for EPM Alloy 39:
5.5Al 8.3Ta 20Co 2Mo
2.3Cr 4.5Ru 5.7Re 5.6W 0.4Ti

1300°C, H₂ anneal:
1100°C Cyclic Oxidation for EPM Alloy 39:
5.5Al 8.3Ta 20Co 2Mo
2.3Cr 4.5Ru 5.7Re 5.6W 0.4Ti

Alloy 39, 1100°C

1300°C, H₂ anneal:
- 100 hr
- 24 hr
- 4 hr
- as-received

1-hr cycles
Reduced Chromium for Single Crystal Superalloys

![Graph showing the relationship between Chromium and Aluminum content for different generations of CMSX alloys. The graph illustrates the trend of chromium content reduction across generations N4, N5, and N6, with CMSX 10, CMSX 4, and CMSX 2 highlighted.](image-url)
Room Temperature, Moisture-Induced Delayed Spallation (MIDS)  
(NASA GRC Anecdotes)

- 1978 NiAl: spalling over beaker of H₂O
- 1986 NiCrAl: sulfur purging (scale ‘washed’ off)
- 1989 PWA 1480: H₂-annealing (breath test)
- 1994 Rene’142, N5: H₂-annealing (immersion test)
- 1998 PWA 1484: melt, H₂-annealing (immersion)
- 2002 René N5: (immersion acoustic emission)
Moisture-Induced Spallation of Al₂O₃ Scales

Additional Key Observations

• 1993, FeCrAl-Ce (Sigler, GM): more spallation in humid air, N₂, Ar

• 1995, René N6 (Smith, Frazier, Pregger, NAWC): scale on high S spalled only in moist O₂/N₂

• 1999, PWA1480, 1484, CMSX4 (Janakiraman, Meier, Pettit, Pitt): spallation for water drop, moist vs dry air

• 2000, FeCrAlY (Tolpygo, Clarke, UCSB): delayed scale buckling in air

• 2003, René N5 (Maris-Sida, Meier, Pettit, Pitt): spallation in high P_{H₂O} air for high sulfur alloy
Delayed TBC Failure
(Weekend Effect, Desk Top Spallation)

• René N5: TBC buckling growth, moisture-assisted subcritical Al₂O₃–bondcoat cracks (1997, Clarke, Christiansen, Tolpygo) (1998, Sergo, Clarke)

• CMSX4: progressive scale debond, TBC failure (2000, Peng, Clarke)

• PWA 1484: ‘no bond coat’ TBC delamination, H₂O immersion (1998, ‘02, ‘04, Smialek)
Undoped Ni$_{15}$Cr$_{13}$Al, Immersion Effects
15 purging cycles, 1120$^\circ$C, 1-hr

As-cooled

After water immersion

(a)  

(b)  5 mm
No Effect of Water Immersion on H$_2$-Annealed Sample

0.01 ppmw S PWA 1484, 1250°C/50 hr Anneal, 1100°C Cyclic Oxidation (10x)
Water Immersion Produces Scale Spallation to Bare Metal
Higher S (1.2 ppmw S) PWA 1484, 1100°C Cyclic Oxidation

200 hr

800 hr

2000 hr

400 hr + H₂O

800 hr + H₂O

2000 hr + H₂O

5 mm
Effect of Sulfur Content on Cyclic Oxidation

PWA 1484 at 1100°C

Oxidation time, 1-hr cycles

Specific
Effect of Sulfur Content on PS NBC TBC Life

PWA 1484 Cyclic Oxidation at 1100°C

Oxidation time, 1-hr cycles

Specific

0 400 800 1200 1600 2000

DTS = desk top spallation

0.25 ppm S
melt de-S

0.01 ppm S
H₂-annealed

1.2 ppm S
as-rec’d

DTS

DTS

DTS

H₂O
(Other side spalled)
Effect of Sulfur Content on TBC Life
PWA 1484, no bond coat, cyclic oxidation at 1100°C

life(h) ≈ \frac{1400}{1 + \left(\frac{S(\text{ppm})}{0.35}\right)^{1.4}}

GDMS sulfur content, ppmw

TBC del

edge failures
(average)
critical S
Substrate and TBC Interface After Delamination (DTS)
High S 1484, no bond coat, 200 hr, 1100 °C Cyclic Oxidation (10x)

First side sprayed

Second side sprayed

5 mm
Overnight Interfacial TBC Failure
Hi S 1484; NBC, 1100°C, 200 hours

5 μm

Metal
Ni
Al Ta
Cr Co

5000X

Al oxide
Idealized Schematic Cross-Sections
(not to scale)

X, grid spacing  10 mils wide

10 mils TBC
10 mils groove
10 mils rib

PWA 1484
Effect of Segmenting by Grooves and Ribs on TBC Durability (1100°C for 2000 h)

A

10 mil deep groove pattern
0.050-0.200" spacing
(vs 200 hr flat side)

B

10 mil high rib pattern,
0.050-0.200" spacing
(vs 150 hr flat side)

1” dia.
Segmented TBC Prevents Failure
U.S. Patent 6,316,078; Nov. 13, 2001

Plasma Sprayed 8YSZ TBC, No Bond Coat, Low Sulfur PWA 1484
10 mil Ribs, 1 in. dia.; Interrupted Oxidation Testing at 1100° C

Flat sides (no ribs) delaminate completely at 400-1000 h
Segmented TBC Prevents Failure
U.S. Patent 6,316,078; Nov. 13, 2001

Plasma Sprayed 8YSZ, No Bond Coat, Low Sulfur PWA 1484
1100°C Cyclic Oxidation, 2000 1-hr Cycles

Flat sides (no ribs) delaminate completely at 400-1000 h
Schematic of TBC (Scale) Buckling Failure
(after H. Evans or A. Evans, et al.)

\[
\sigma_b = \frac{1.22 E_{TBC}}{1 - \nu^2} \left( \frac{h_{TBC}}{r_b} \right)^2
\]

\[
\sigma_{cte} = \frac{\left( \Delta a_{cte} \Delta T \right) E_{TBC}}{(1 + R)(1 - \nu_{TBC})}
\]
Effect of Ribbed TBC Segment Size on Life
10 mil 8YSZ, No Bond Coat, Low S PWA 1484

E = Edge delamination
(no ribs)

no failure

Segment size, D

Buckling life, \( t_f \), hr

1150°C, 1100°C

100 hr cycles

1 hr cycles

\( 2R_{B, 1150} \)

\( 2R^*_{B, 1100} \)
Effect of Moisture Exposure after Cyclic Oxidation of Rene 142 at 1150

Σ moisture-induced loss (breath effects)

net sample weight

immersion

R142-8, 1 mm
1280°C, 100 hr, 1 atm H₂
Interfacial spalling for 1150 °C oxidation of as-received René 142. No anneal; moisture treatment (R142-6, 1 mm, 6.1 ppm S). (a) 40 hr. (b) 80 hr. (c) 100 hr. (d) 140 hr. (e) 180 hr. (f) 200 hr. (g) 500 hr. (h) 1000 hr.
Interfacial spalling for 1150 °C oxidation of annealed René 142. 1280 °C/100 hr H/A; moisture treatment (R142-8, 1 mm, 0.3 ppm S). (a) 40 hr. (b) 60 hr. (c) 80 hr. (d) 100 hr. (e) 140 hr. (f) 180 hr. (g) 200 hr. (h) 500 hr. (i) 1000 hr.
Interfacial spalling for 1150 °C oxidation of annealed René N5 (+Y). 1280 °C/100 hr H/A; moisture treatment (N5-2, 3 mm, 3.7 ppm S). (a) 20 hr, side b. (b) 80 hr, side b. (c) 100 hr, side b. (d) 140 hr, side b. (e) 180 hr, side d. (f) 200 hr, side d. (g) 500 hr, side d. (h) 1000 hr, side d.
Effect of Y Content and H₂ Annealing on Final Weight Change
(Rene'N5 after 1000 1-hr Cycles at 1150°C)
The Effect of Y/S Ratio on Oxidation Behavior

(Rene'N5 oxidized at 1150° for 1000 1-hr cycles)

Yttrium / Sulfur ratio, ppma/ppma

H₂-annealed
as-received

PWA 1484
(Aimone, 1992)

YS

Y₂O₂S

Y₂S₃

1000 hr.

Yttrium / Sulfur ratio, ppma/ppma
Effect of Water Immersion on Spalling

(Rene'N5 after 500 1-hr Cycles at 1150°C)

Y Levels, ppmw

spall due to

as-received
H₂-annealed

0 16 24 31 48 53 67 88 103 105

Y Levels, ppmw
Effect of Water Immersion on Spallation
Rene’N5+103Y, 1150°C, 500 hr

as-received
bare metal spalling
after immersion

as-cooled

no spalling
H₂-annealed
1150°C Cyclic Oxidation of Rene'N5

(1250°C, 100 hr H₂)

-40.6 mg/cm² @ 1000 hr

H₂O

H₂ annealed

0 Y, <0.01 S

0 Y, 2.6 S

as-received

www.nasa.gov
Immersion Effect for Rene’N5 (+Y)
1150°C, 1-hr cycles, ±Y, H-annealing

(1250°C, 100 hr H₂)

H₂ annealed

H₂O

50 Y, 5.4 S

(50 Y, 6.2 S (ppmw))

H₂O

2000
Moisture-Induced Delayed Spallation (MIDS)
Acoustic Emission during Immersion
(pre-oxidized Rene’N5+Y, 1000 1-hr cycles @ 1150°C)

G.N. Morscher, 2000
EB-PVD 7Y$_2$O$_3$-ZrO$_2$ TBC
Ni(Pt)Al bond coat, Rene’N5,
Laser HHFT, 1280/1050$^\circ$C, 200x2 hr

Zhu, 2001
Delayed Desk Top Failures of EB PVD TBC

Ni(Pt)Al bond coat on Rene’N5; 1135°C

360-720 cycles to failure; 45 min/ hot cycle

Zhu, 2005
A large portion of the TBC failure is at the scale-metal interface.
Moisture-Induced Delayed Failure
EB-PVD RE-YSZ, Ni(Pt)Al, Rene N5, 1150ºC, 300 cycles

Oct. 10, 2006
Slow (Subcritical) Crack Growth (?)

In bulk Al$_2$O$_3$:  

- $v_c \approx 10^{-6}$ to $10^{-3}$ m/s
- $\text{Al}_2\text{O}_3 + 3 \text{H}_2\text{O} = 2\text{Al(OH)}_3$

For Al$_2$O$_3$ scale – NiCrAl interface:  
(Acoustic emission, Smialek-Morscher, 2002)

- $v_c \approx 10^{-3}$ to $10^2$ m/s
- $\text{Al} + 3 \text{H}_2\text{O} = \text{Al(OH)}_3 + \frac{3}{2} \text{H}_2$
Ambient Moisture-Induced Hydrogen Embrittlement of Intermetallics  
(compelling analogy to delayed scale spallation)

• Extrinsically brittle M₃X compounds: (Ni,Fe,Co)₃(Al,Si,Ti)

• Embrittled by moist air, not dry O₂, or vacuum:
  \[2\text{Al} + 3\text{H}_2\text{O} = \text{Al}_2\text{O}_3 + 6\text{H}^+\]
  \[\text{or Al} + 3\text{H}_2\text{O} = \text{Al(OH)}_3 + 3\text{H}^+\]

• Max effect near room temperature

• Only at slow vs high strain rates

(Stoloff et al., Liu et al.) 
1994 MRS Keynote Lecture
“...crack propagation is a discontinuous process... 
...further growth must await diffusion of hydrogen... 
...the plateaus...are the ‘secondary’ incubation periods...”
Fig. 11. Resistance Increase as a Function of Time For Uniformly Hydrogenated Specimens Tested in the Stress Range of Delayed Failure (Troiano, 1959)
## Hydrogen Embrittlement and Moisture-Induced Delayed Failures (steels, Ni-alloys, aluminides)

<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>Sulfur segregation</td>
<td>Intergranular embrittlement</td>
<td>✓ Interfacial weakening</td>
</tr>
<tr>
<td>Theoretical strength</td>
<td>H, S decrease M-M bond</td>
<td>✓ H, S decrease M-Al₂O₃ bond</td>
</tr>
<tr>
<td>Moisture effects,</td>
<td>Intergranular and cleavage</td>
<td>✓ Interfacial weakening</td>
</tr>
<tr>
<td>Hydrogen diffusion,</td>
<td>Delayed failure at Rm Temp.</td>
<td>✓ Delayed Rm Temp. failure</td>
</tr>
<tr>
<td>Tensile stress state</td>
<td>Intermittent crack growth</td>
<td>✓ Intermittent spallation</td>
</tr>
<tr>
<td>H + S segregation</td>
<td>Negative synergy</td>
<td>? Negative synergy</td>
</tr>
<tr>
<td>Cathodic charging</td>
<td>H-embrittlement</td>
<td>? Interfacial de-scaling</td>
</tr>
</tbody>
</table>

**Occam’s Razor:** keep it simple and draw from known experience
Critical experiment:
Test whether hydrogen charging causes scale delamination (e.g., H-embrittlement of Ni$_3$Al+B, Kuruvilla, Stoloff, 1985)
**H₂ blisters**

-2.0 V

**De-scaling**

0.0 V

**No effect**

+2.0 V

**Dissolution**

<table>
<thead>
<tr>
<th>Applied Potential, V</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>-3.0 V</td>
<td>H₂ blisters</td>
</tr>
<tr>
<td>-2.0 V</td>
<td>De-scaling</td>
</tr>
<tr>
<td>0.0 V</td>
<td>No effect</td>
</tr>
<tr>
<td>+2.0 V</td>
<td>Dissolution</td>
</tr>
</tbody>
</table>
Exposed Ni(CrAlWCo) substrate

Oxide imprints (SE) in exposed metal

-2.0 V

Cathodic De-Scaling of Rene’N5
1 hr @ -2.0 V in 1N H₂SO₄

Exposed metal

Pt

HfO₂

TaC

Al₂O₃

Al₂O₃

Al₂O₃
Cathodic Hydrogen Cracking and Blistering

\[ \gamma' \text{ etching bare Rene’N5, } -3.0\text{V, } 1\text{ N }\text{H}_2\text{SO}_4 \]
Moisture-Induced Hydrogen Embrittlement: Delayed $\text{Al}_2\text{O}_3$ (and Desk Top TBC) Spallation

$\text{H, S, (C?)}$ synergistic weakening

Spalled

$3\text{H}_2\text{O}$

$\text{Al}^{+++}(\text{OH})_3^-$

$3\text{H}^+$

$\text{YSZ TBC}$

Intact

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

Incubation

Substrate

$\tau_{\text{spall3}} << \tau_{\text{incubate2}} << \tau_{\text{intact1}}$

$cathode$

$anode$

$\sigma_{\Delta \text{CTE}}$

$\sigma_{\Delta \text{CTE}}$

unzipping interface
Summary of MIDS Phenomenology (caveats)

- Intermediate sulfur content
- Mature, cycled (damaged) scales (with exposed interface to humid environment)
- Water immersion as accelerated test
- Increases spallation, but may not be necessary
- H-charging failed adherent, but mature scales
- (Stabilization for intermediate PH2O aging?)
Connections and Proposed Hypothesis

1. **Primary** scale (TBC) chemical effect due to sulfur.

2. **Secondary**, delayed Al₂O₃ scale (and TBC) spallation = *moisture* effects (MIDS, DTS).

   Cathodic **H-charging** causes massive interfacial Al₂O₃ scale spallation at very low current (1mA at -2V).

:::Interfacial hydrogen embrittlement is responsible for moisture-induced delayed failure of Al₂O₃ scales and thus contributes to Desk Top Spallation of TBC’s.
• PWA 1484, Rene’142, Rene ’N5
  – Critical Y/S ratio ~ 1:1 atomic (3:1 by weight)
  – H₂-anneal improves adhesion (cyclic + immersion)
  – Evidence that moisture-assisted spallation, is a hydrogen embrittlement phenomenon
Cyclic Oxidation Modeling:

\[ \frac{\Delta W}{A} = f(\sqrt{k_1 t}, k_2 t) \]

- \( + \sqrt{k_1 t} = \text{growth} \)
- \( - k_2 t = \text{spallation} \)

paralinear model fitting

\[ \Delta W/A \]
Cyclic Oxidation Modeling
Basic Features

• Postulate an oxide:
  \( \text{Al}_2\text{O}_3, \text{NiO,} \ldots \); \( S_c = \text{mass oxide/oxygen} \)
• Define the kinetic growth behavior:
  (parabolic \( k_p \), power law \( k, m \)\ldots)
• Define the spalling algorithm:
  (% spall = \( Q_o \cdot \text{existing scale}^\alpha \)
  (outer layer vs bare metal segments)
• Perform iterative calculations; bookkeeping
  oxygen gain, oxide lost, metal consumed,\ldots
### Cyclic Oxidation Modeling

**Common Variations (COSP)**

<table>
<thead>
<tr>
<th>GROWTH</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>parabolic</strong></td>
<td>( (\Delta \frac{W}{A})^{2} = k_{p} t )</td>
</tr>
<tr>
<td>(oxygen mass gain)</td>
<td></td>
</tr>
<tr>
<td><strong>power law</strong></td>
<td>( (\Delta \frac{W}{A})^{m} = k_{p} t )</td>
</tr>
<tr>
<td><strong>logarithmic</strong></td>
<td>( (\Delta \frac{W}{A}) = \ln \left( (kt + c) \right)^{\frac{1}{m}} )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SPALL FRACTION</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SPALLATION</strong></td>
<td></td>
</tr>
<tr>
<td><strong>uniform thickness</strong></td>
<td>( F_{S} = Q_{o} W^{\frac{\alpha}{r}} ); ( \alpha = 1 )</td>
</tr>
<tr>
<td>(oxide mass loss)</td>
<td></td>
</tr>
<tr>
<td><strong>Monte Carlo (bimodal)</strong></td>
<td>( F_{S} = Q_{o} W^{\frac{\alpha}{r}} ); ( \alpha = 1 )</td>
</tr>
<tr>
<td><strong>DICOSM</strong></td>
<td></td>
</tr>
<tr>
<td>( F_{A} = \text{spall area fraction} ) (thickest segment)</td>
<td></td>
</tr>
<tr>
<td>( p - k_{p}; \text{(Monceau)} )</td>
<td>( p = \text{spall (area) probability} )</td>
</tr>
</tbody>
</table>
Schematic of Deterministic Interfacial Spalling Model

A) cycle number, \((j)\), less than number of area segments, \((n_o)\)

- **Cycle**
  - \(j = 1\)
    - \(i = 1\)
  - \(j = 2\)
  - \(j = 3\)
  - \(j = 4\)
  - \(j = 5\)

- Intact oxide
- Spalled oxide

- \(F_A = \frac{1}{10}\)
- \(F_A = \frac{1}{n_o}\)

- \(i = 1\) to \(i = 2\) to \(i = 3\) to \(i = 4\) to \(i = 5\) to \(i = 6\) to \(i = 7\) to \(i = 8\) to \(i = 9\) to \(i = 10 = n_o\)
1. Uniform
2. Monte Carlo
3. DICOSM
COSP Model Outputs

$\text{Al}_2\text{O}_3$ scale, $k_p = 0.01$ mg/cm$^2$, $\Delta t = 1$ hr,
$Q_o = 0.002$ cm$^2$/mg, $\alpha = 1.0$
Parametric Study: Effect of $k_p$ (parabolic, Al$_2$O$_3$, $Q_o=0.002$, $\Delta t=1$ hr)

$k_p$ (mg/cm$^2$/hr)

- 0.001
- 0.002
- 0.005
- 0.010
- 0.020
- 0.050

specif

1-hr cycles
Semi-universal Cyclic Oxidation Curve (DICOSM-GSA model)

Normalized cycle number, \( J_u = j / j_{\text{max}} \)

\[ W_u = \frac{1}{2} \left[ 3J_u^{1/2} - J_u^{-3/2} \right] \]

Normalized weight, \( W = (WA)^{1/2} \)
Effect of Sulfur Content on the 1100°C Cyclic Oxidation of PWA 1480
(DICOSM fit: dashed lines)
Universal Cyclic Oxidation Life Map
PWA 1480, 1100°C

Criteria:

Universal Cyclic Oxidation Life Map
PWA 1480, 1100°C

Sulfur, ppmw
6.7
3.9
1.5
0.8
0.12

ΣW_{Al} failure locus
10 mg/cm², 1000 h

excessive spallation

minimal growth and spallation

normalized k_p,
\{j*k_p\Delta t(S_c^{-1})^2/(3/4\Sigma W_{m}^*)^2\}
Cyclic Models

- User-friendly COSP for Windows (multiple models, instant plots, uploads expt'l data)
- Produce typical plots; fits ideal alloy behavior
- DICOSM, p-k, allow analytical solutions, trends, universal failure maps.
1. About 0.2 ppmw S (or Y/S ratio of 1:1) is critical.
2. Interfacial hydrogen embrittlement causes moisture-induced delayed failure (MIDS) of Al₂O₃ scales.
3. Ideal cyclic behavior can be analyzed by models.


