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 H₂O = 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>
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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
- $\text{Cr}_2\text{O}_3$ (?), $\text{NiCr}_2\text{O}_4$, $\text{NiO}$, $\text{TiO}_2$, $\text{HfO}_2$ 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>ΔW/A</th>
<th>Al</th>
<th>Cr</th>
<th>Ti</th>
<th>Ta</th>
<th>Nb</th>
<th>Mo</th>
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### 1100°C, 200 hr

|          | mg/cm² |       |     |
|----------|--------|-------|
| avg      | 7.04   |       |
| stdev    | 0.69   |       |
Inverse Correlation of Aluminum and Chromium in 25 Superalloys

Al + 0.22 Cr = 7.25

$\text{r}^2 = 0.70$
Predicted Cyclic Oxidation Weight Change
Ni-(6Co-6Al-6Cr-6Ta)-(1Ti-1Nb-1Mo-1W)-(0.2Hf-0.1C)
Diffusion Controlled Desulfurization

\[ \text{oxide-free surface} \]

\[ \text{S diffusion} \]

\[ C_S \sim \frac{D_S t}{L^2} \]

\[ \text{superalloy coupon} \]
Effect of Sulfur Content on the 1100°C Cyclic Oxidation of PWA 1480

oxidation time, 1-hr cycles

weight loss (ppmw S)
Oxide Adherence Map for Desulfurized PWA1480

1100 C, 1-hr Cycles, 500 Hours

Sulfur content, $C_s$, ppmw

Sample thickness, mm

mg/cm$^2$

- $< -30$
- $-20/-30$
- $-10/-20$
- $-5/-10$
- $-1/-5$
- $+1/-1$

Non-adherent

Adherent
• **PWA 1480**
  
  – Distinct *critical sulfur content* and thickness effect
  
  – $\approx 0.2 \text{ ppmw } S$ @ 1 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
1484, 0.01 S
1480, 0.2 S
Improved 1100°C Cyclic Oxidation
Rene’N4 to N5±Y, N6

1-hr cycles

Rene' N4
Rene' N5-
Rene' N6

N4
(4Al 4Ti)

N5,6
(6Al)
Exceptional 1150°C Cyclic Oxidation: PWA 1484 and Rene’N5

1-hr cycles

Rene’N5 - (ca. 1992) Rene’N5 -, H2-annealed, 1200°C / 100 hr PWA1484, PCC melt desulfurized, (ca. 1998) 0.3 ppmw S

N5-, H2 ~0.3 S

1484 melt deS 0.3 S

~3 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:
- 100 hr
- 24 hr
- 4 hr
- as-received
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:
- 100 hr
- 24 hr
- 4 hr
- as-received
Reduced Chromium for Single Crystal Superalloys

Chromium, wt. %

Aluminum w%

CMSX 10
CMSX 4
CMSX 2
EPM102

1480
1484
1480

N6
N5
N4

generation

conventional SA
SA regression
SXSA

www.nasa.gov
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 Al$_2$O$_3$–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, H$_2$O immersion (1998, ‘02, ‘04, Smialek)
Undoped Ni15Cr13Al, Immersion Effects
15 purging cycles, 1120°C, 1-hr

As-cooled

After water immersion
No Effect of Water Immersion on H₂-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

H₂O

H₂O

0.01 ppm S
H₂-annealed

0.25 ppm S
melt de-S

1.2 ppm S
as-rec’d

1.2 ppm S
as-rec’d
Effect of Sulfur Content on PS NBC TBC Life

PWA 1484 Cyclic Oxidation at 1100°C

Oxidation time, 1-hr cycles

Specific

DTS = desk top spallation

0.01 ppm S H₂-annealed

0.25 ppm S melt de-S

1.2 ppm S as-rec'd

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

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

edge failures
(average)

critical S

GDMS sulfur content, ppmw
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

5000X

metal

Ni

Al Ta

Cr Co

oxide

Al
Idealized Schematic Cross-Sections
(not to scale)

X, grid spacing  10 mils wide

10 mils TBC

10 mils groove

10 mils TBC

10 mils rib

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

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

10 mil high rib pattern, 0.050-0.200" spacing (vs 150 hr flat side)
Plasma Sprayed 8YSZ TBC, No Bond Coat, Low Sulfur PWA 1484
10 mil Ribs, 1 in. dia.; Interrupted Oxidation Testing at 1100° C

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

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

Buckled, 2000 h 0.5 in. rib spacing
No Buckle, 2000 h 0.25 in. rib spacing
No Buckle, 2000 h 0.125 in. rib spacing

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

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

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

- 1150°C
- 1100°C

- E = Edge delamination (no ribs)
- 100 hr cycles
- 1 hr cycles
- no failure

Segment size, D

Buckling life, tₙ, hr
Effect of Moisture Exposure after Cyclic Oxidation of Rene'142 at 1150°C

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 Y Content and H₂ Annealing on Final Weight Change
(Rene'N5 after 1000 1-hr Cycles at 1150°C)

Y levels, ppmw
0 16 24 31 48 53 67 88 103 105

as-received
H₂-annealed
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)

Y₂S₃
YS
Y₂O₂S

0 1 2 3 4 5 6 7 8
0 10

1000 hr. vs.

Yttrium / Sulfur ratio, ppma/ppma
Effect of Water Immersion on Spalling
(Rene'N5 after 500 1-hr Cycles at 1150°C)

![Graph showing the effect of water immersion on spalling with Y levels in ppmw. The graph compares as-received and H₂-annealed samples.](image-url)
Effect of Water Immersion on Spallation
Rene’N5+103Y, 1150°C, 500 hr

- as-received
  - bare metal spalling
  - after immersion
- as-cooled
- H₂-annealed
  - no spalling
1150°C Cyclic Oxidation of Rene'N5
(1250°C, 100 hr H₂)

2

H₂O

H₂O (ppmw)

0 Y, <0.01 S

H₂ annealed

-40.6 mg/cm² @ 1000 hr

specif

1-hr cycles

-2.0

0 200 400 600 800 1000

as-received

0 Y, 2.6 S

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

(1250° C, 100 hr H₂)

H₂ annealed

50 Y, 5.4 S

50 Y, 6.2 S (ppmw)

H₂O

H₂O
Moisture-Induced Delayed Spallation (MIDS)
Acoustic Emission during Immersion
(pre-oxidized Rene’N5+Y, 1000 1-hr cycles @ 1150oC)

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

7YSZ

Al$_2$O$_3$ scale

Bond coat

1280°C

1050°C

30 μm

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, 1150°C, 300 cycles

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

**In bulk Al₂O₃:**


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

**For Al₂O₃ scale – NiCrAl interface:**

(Acoustic emission, Smialek-Morscher, 2002)

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

\[
2\text{Al} + 3\text{H}_2\text{O} = \text{Al}_2\text{O}_3 + 6\text{H}^+ \\
\text{[or Al} + \text{3H}_2\text{O} = \text{Al(OH)}_3 + 3\text{H}^+] \\
\]

• Max effect near room temperature

• Only at slow vs high strain rates

(Stoloff et al., Liu et al.)
1994 MRS Keynote Lecture
Intermittent Nature of Crack Growth in Hydrogen Embrittled High Strength Steel

“...crack propagation is a discontinuous process... further growth must await diffusion of hydrogen... the plateaus...are the ‘secondary’ incubation periods...”

A.R. Troiano, Chairman, Dept. of Metallurgy
Case Institute of Technology
1959 Edward de Mille Campbell Lecture, ASM
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)

## Common Features

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

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**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 Ni₃Al+B, Kuruvilla, Stoloff, 1985)

Standard Electrochemical Cathodic Hydrogen Charging

Anodic: +1.3V, H₂
Cathodic: -2.0V, A.R.
H$_2$ blisters to -3.0 V

De-scaling to -2.0 V

No effect at 0.0 V

Dissolution to +2.0 V

Graph showing the effects of applied potential on various phenomena:

- Massive cathodic de-scaling
- Anodic dissolution and pitting
- Tarnish film
- N$_5$ blisters and cracks

Potential range: -3.0 V to +2.0 V
Cathodic De-Scaling of Rene’N5
1 hr @ -2.0 V in 1N H₂SO₄

Exposed metal

Oxide imprints (SE) in exposed metal

TaC

Al₂O₃

Pt

HfO₂

Al₂O₃

Exposed metal

Al₂O₃

200μm

20.0μm

67-1 15.0kV 14.1mm x2.50k GWBSE 7/7/2005

67-1 15.0kV 14.1mm x2.50k GWBSE 7/7/2005
Cathodic Hydrogen Cracking and Blistering

γ’ etching bare Rene’N5, -3.0V, 1 N H₂SO₄
Moisture-Induced Hydrogen Embrittlement: Delayed Al₂O₃ (and Desk Top TBC) Spallation

Spalled

3

Al⁴⁺⁺⁺(OH)₃⁻

3H⁺

3H₂O

H, S, (C?) synergistic weakening

YSZ TBC

Intact

1

Substrate

Incubation

2

cathode

unzipping interface

e⁻

anode

τₚₚₙₐₖ₃ \ll τₚₙₐₖₑ₃ \ll \ll τₚₙₐₖₑ_{intact1}

σ_{ΔCTE}

σ_{ΔCTE}
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 $P_{H_2O}$ aging?)
Connections and Proposed Hypothesis

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

2. **Secondary**, delayed $\text{Al}_2\text{O}_3$ scale (and TBC) spallation = moisture effects (MIDS, DTS).

Cathodic **H-charging** causes massive interfacial $\text{Al}_2\text{O}_3$ scale spallation at very low current (1mA at -2V).

**.:** Interfacial hydrogen embrittlement is responsible for moisture-induced delayed failure of $\text{Al}_2\text{O}_3$ scales and thus contributes to Desk Top Spallation of TBC’s.
• **PWA 1484, Rene’142, Rene ’N5**
  – *Critical Y/S ratio* \( \sim 1:1 \) *atomic* \( (3:1 \) by weight)\)
  – \( H_2 \)-anneal improves adhesion
    (cyclic + immersion)
  – Evidence that *moisture-assisted spallation*,
    is a *hydrogen embrittlement* phenomenon
Cyclic Oxidation Modeling:

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

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

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 \(k, m\)…)

• 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,…
# Cyclic Oxidation Modeling
## Common Variations (COSP)

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

<table>
<thead>
<tr>
<th>SPALL FRACTION</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>SPALLATION</td>
<td>uniform thickness</td>
<td>( F_S = Q_o W^{; r; \alpha} ; \alpha = 1 )</td>
</tr>
<tr>
<td>(oxide mass loss)</td>
<td>Monte Carlo (bimodal)</td>
<td>( F_S = Q_o W^{; r; \alpha} ; \alpha = 1 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( R_{spall} = \frac{\text{spall depth}}{\text{total scale thickness}} )</td>
</tr>
<tr>
<td>DICOSM</td>
<td></td>
<td>( F_A = \text{spall area fraction} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(thickest segment)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( p = \text{spall (area) probability} )</td>
</tr>
</tbody>
</table>

\( p \cdot k_p \); (Monceau)
Schematic of Deterministic Interfacial Spalling Model

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

- Cycle number: 1 2 3 4 5 6 7 8 9 10 = \( n_o \)
- FA = spall area fraction, \( = 1/n_o \)

- Intact oxide
- Spalled oxide

FA = 1/10
1. Uniform
2. Monte Carlo
3. DICOSM
COSP Model Outputs

$\text{Al}_2\text{O}_3$ scale, $k_p = 0.01 \text{ mg/cm}^2$, $\Delta t = 1 \text{ hr}$, $Q_o = 0.002 \text{ cm}^2/\text{mg}$, $\alpha = 1.0$
Parametric Study: Effect of $k_p$
(parabolic, $\text{Al}_2\text{O}_3$, $Q_0=0.002$, $\Delta t=1$ hr)
Normalized cycle number, $J_U = j/j_{\text{max}}$

Normalized weight, $W_u = \frac{W}{A}$

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

\[ \{ j k_p \Delta t (S_c - 1)^2 / (3/4 \Sigma W_m^*) \} \]

Normalized \( k_p \),

Normalized spallation

excessive growth

Sulfur, ppmw

\[ 6.7 \]
\[ 3.9 \]
\[ 1.5 \]
\[ 0.8 \]
\[ 0.12 \]

\( \Sigma W_{Al} \) failure locus

10 mg/cm², 1000 h

minimal growth and spallation

excessive spallation

www.nasa.gov
• **Cyclic Models**

  – User – friendly COSP for Windows  
    (multiple models, instant plots, uploads expt’l data)
  – Produce typical plots; fits ideal alloy behavior
  – DICOSM, p-\(k_p\) allow analytical solutions, trends,  
    universal failure maps.
Final Recap

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 Al$_2$O$_3$ scales.
3. Ideal cyclic behavior can be analyzed by models.


