An Overview of Plutonium Aging

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Objectives

- Provide advance warning of manufacturing & aging defects
- Provide a *predictive* lifetime assessment for safety & reliability at a minimum age of 45-60 years

Approach – Implementing Predictive Science

- Identify Key Material Properties
- Measure properties at zero-age
- Identify aging signatures for key properties and model
  - Accelerate where possible
- Measure aged material, refine models
- Define Thresholds of acceptable change
- Lifetime is defined by point when property reaches limit of acceptable change.

Illustration of alpha-decay in delta Pu, Wolfer (2001)
Timescales for Plutonium Aging

Understanding Materials
Aging is Key for Prediction of Lifetimes

Material Properties

Microstructure

Atomic structure

Component Properties

Cumulative Change

void swelling

Δt

establish equilibrium in lattice damage

Atomic structure

He ingrowth

surface corrosion

He bubble formation?

phase stability

Microstructure

Atomic structure

establish equilibrium in lattice damage

Atomic structure

He ingrowth

surface corrosion

He bubble formation?
Key Properties and Aging Mechanisms

Key Plutonium Properties

- Density
- Compressibility
- Strength
- Corrosion Resistance

Corrosion of Metallic Pu in a defective Storage Container
(Haschke and Martz, Plutonium Storage 1998)

Important Potential Aging Mechanisms

- Self-Irradiation Damage
  - He ingrowth
  - change in chemistry
  - atomic displacements from recoil atoms
- Phase Stability
- Surface Corrosion

Simulation of radiation damage in delta-Pu
• Chemistry continually changes
  • He ingrowth
    • Potential for bubble growth
  • Am buildup
    • Reaches secular equilibrium in few decades
  • U, Np other important products
Aging Mechanisms – Self Irradiation

α-decay event

- $^{239}$Pu: α-decay: $t_{1/2} = 24,000$ yr
  - 2.3 x 10$^9$ a events/gram/s

- Primary defect production (100 ps)
  - Collision cascade with clustering & recombination
  - ~ 20,000 displacements/event
  - ~ 90% immediately recombine
  - ~ 2500 Frenkel pairs/event
  - 0.1 displacements/atom/year (dpa)

**Aging Mechanisms – Self Irradiation**

Void swelling is potentially the most important result of self irradiation. The biggest unknown is the magnitude of the incubation period for void swelling.

- Experimental evidence exists for the initial lattice parameter change, and for helium bubble swelling.
- No clear evidence for onset of void swelling

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**Dimensional Change, \( \frac{dV}{V} \)%**

- **Total**
- **He Accommodation in Vacancies**
- **Radiation Damage**
- **Accumulation and Saturation of Cascade Damage**
- **Start of Void Swelling ?**


R. Mulford, unpublished data, 2003

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**Fraction of DamagedFelitan**

- Annealing Temperature (°K)

Mark Weill and Salem Schwartz (LLNL)
Aging Mechanisms – Self Irradiation

Calculation of displacement requires detailed knowledge of both bond energies and defect structures.

This requires a detailed understanding of f-electrons – a most challenging task!

- The transition from delocalized to localized 5f electrons (Mott-like) takes place at Pu
- Pu appears to undergo an intermediate transition that is only partly localized!

Wills, Eriksson, 2000, Los Alamos Science, 26, 128
PES measurement

$\delta$-Pu 0.5 wt.% Ga

$h_v = 40.8$ eV

$T = 77$ K

$\Delta E \sim 60$ meV

Intensity (Arb. units)

Binding Energy (eV)

**New Developments in Electronic Structure Calculation**

- Photoemission data taken at a photon energy of 40.8 eV.
- Matrix element calculations between the initial and final states using a photon energy of 40.8 eV.
- One-electron calculations fail to account for 5f electron correlations
- Electronic structure calculation using the constrained GGA or mixed-level model (MLM) with 4 of the 5 Pu 5f electrons localized.

J.J. Joyce, L.A. Morales & J.M. Wills
Aging Effects: Phase Stability


Aging Effects: Phase Stability

The $\delta \rightarrow \alpha'$ Transformation in Pu-0.5 wt. % Ga

- Composition
- Microstructure
- Thermal history
- Processing
- Aging

Dilatometry

$\alpha' \rightarrow \delta$ reversion
Closely spaced bursts.

$25 \, ^\circ\text{C} \rightarrow -155\, ^\circ\text{C} \rightarrow 25 \, ^\circ\text{C}$

J. Mitchell, R. Pereyra
Phase Stability: XAFS Results and Local Order

- Unaged alloys near metastable composition range higher degree of disorder
- Aged materials or high stabilizer concentration show higher degree of order
- Radiation damage may redistribute Ga with age

**EXAFS Fourier Transform**

0.75 wt% Ga, unaged

0.5 wt% Ga, 10-15 yrs

1.0 wt% Ga, 20 yrs

1.0 wt% Ga, 32 yrs

(Data) - (fit to fcc structure)

S.D. Conradson, L.E. Cox, B. Martinez, L. Morales and R.A. Pereyra
Phase Stability: elastic constants as an early indicator

- Can determine full elastic tensor for EOS
- Phase stability (α-δ transition) can readily be observed using RUS
- Real-time aging effects probed
  - \( t = 0 \text{y}; \ B = 29.6 \text{ GPa} \)
  - \( t = 15 \text{y}; \ B = 34.3 \text{ GPa} \)

\[ \Delta \frac{c_{11}}{c_{11}} \quad \Delta \frac{c_{44}}{c_{44}} \]

\[ \Delta \frac{c_{11}}{c_{11}} \quad \Delta \frac{c_{44}}{c_{44}} (\text{ppm}) \]

\[ \begin{array}{c}
-0.50 \\
-0.40 \\
-0.30 \\
-0.20 \\
-0.10 \\
0.00 \\
0.10 \\
0.20 \\
0.30 \\
0.40 \\
0.50 \\
0.60 \\
0.70 \\
0.80 \\
0.90 \\
1.00 \\
\end{array} \]

\[ \begin{array}{c}
300 \\
350 \\
400 \\
450 \\
500 \\
550 \\
\end{array} \]

\[ \begin{array}{c}
0 \\
50 \\
100 \\
150 \\
200 \\
250 \\
\end{array} \]

\[ 3.8 \text{ ppm/h} \quad 6.5 \text{ ppm/h} \]

\[ 4.1 \text{ ppm/h} \]

\[ \text{glovebox bump} \]

A. Migliori, J. Baiardo, B. Martinez, and R.A. Pereyra
Surface Corrosion: hydrogen-catalysis accelerates reaction

- Hydride-catalyzed reactions are potentially catastrophic
  - high rates can be useful for recovery or processing of metallic Pu
- Pyrophoric behavior at elevated temperatures (>500 °C)
- Prevent by 2-methods:
  - seal containers
  - exclude organics

Haschke, Allen, Morales, 2000, Los Alamos Science, 26, 252
Surface Corrosion: the complexity of surface oxides

Photoemission: $O_2$ on $\delta$-Pu

$\delta$-Pu with $O_2$ dosing
LPLS data $h\nu=40.8$ eV

Energy (eV)

$-12$ $-10$ $-8$ $-6$ $-4$ $-2$ $0$

Pu$_2$O$_3$
PuO$_2$

$25^\circ\text{C/Vacuum}$
PuO$_2$
Pu$_2$O$_3$
Pu

months

Room T
PuO$_2$
Pu$_2$O$_3$
Pu

Pu

$150^\circ\text{C/Vacuum}$
Pu$_2$O$_3$
Pu

minutes

J.J. Joyce & L.A. Morales
Surface Corrosion: catalyzed oxidation

Catalyzed oxidation in storage has lead to container failure and breach

- small molecule reactions have led to stoichiometry changes, containment breaches and dispersal of material (safety concern)

\[
\text{PuO}_2(s) + x\text{H}_2\text{O} \rightarrow \text{PuO}_{2+x}(s) + \text{H}_2(g)
\]

- PVT, TGA microbalance, MS, and XRD studies suggest formation of a higher oxide

Conclusions

- Virtually all conditions in Pu are “ripe” for aging damage
- Yet, we have found no first-order effects after decades
- Surface reactions are potentially most catastrophic
- Phase stability is still a concern over full range of expected conditions, especially for some alloys
- We are beginning to measure lattice damage and helium accumulation effects
- Void swelling may cause largest density change - incubation period is very sensitive to defect structure
- We still have very little information on mechanical properties and dynamic response
- He in-growth is still a concern, especially at extended ages

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