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Title: Plutonium Metallurgy

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Intended for: Seaborg Institute Student Seminar

Plutonium Metallurgy

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Los Alamos, NM
August 9, 2012

Reference Materials:

Plutonium Metallurgy at Los Alamos, 1943-1945: Recollections of Edward F. Hammel,
E.F. Hammel, Self-published in 1998.

General Metallurgy
Structure of Metals, Third Edition: Crystallographic Methods, Principles and Data (International Series on Materials Science and Technology), C.S. Barrett and T. B. Massalski

Phase Transformations in Metals and Alloys, 3rd Edition; D. A. Porter, K.E. Easterling, M. Sherif

Physical Metallurgy Principles (Prindle, Weber & Schmidt Series in Advanced Mathematics)
R. Abbaschian, R.E. Reed-Hill

Plutonium and Other Actinides
Challenges in Plutonium Science (Los Alamos Science, Vol. 1 and 2, Number 26), N.G. Cooper

"Plutonium," Chapter 7, The Chemistry of the Actinides and Transactinides, 3rd Edition, Springer, D.L. Clark, S.S. Hecker, G.D. Jarvinen, and M.P. Neu,

The Metal Plutonium (University of Chicago Press), A.S. Coffinberry, W.N. Miner

The Series: **Plutonium 1960**, **Plutonium 1965**, **Plutonium 1970**, and **Plutonium 1975**

Phase Diagrams of Binary Actinide Alloys (ASM Monograph Series on Alloy Phase Diagrams)
M. E. Kassner, D. E. Peterson

Plutonium Handbook : A Guide to the Technology, Vol. 1 and 2, O. J. Wick

Reference Materials: (cont.)

Plutonium Metallurgical Reports:

Physical and Mechanical Metallurgy Studies On Delta Stabilized Plutonium-Gallium Alloys (BNWL- 13, UC- 25), H. R. Gardner (April, 1965), Battelle-Northwest/Pacific Northwest Laboratory,

Plutonium Metallurgy Notebook (BNWL- 37, UC- 25), M. E. Hasbrouck, (September, 1965) Battelle-Northwest/Pacific Northwest Laboratory,

Plutonium Microstructures Part 1 “Impurities and Inclusions” (UCRL-53174-1, 1981) and Part 2 “Binary and Ternary Alloys” ” (UCRL-53174-2, 1983) , E.M. Cramer and J.B. Bergin, Lawrence Livermore National Laboratory

Miscellaneous Report Archive Websites:

http://lasearch.lanl.gov/oppie/service - LANL Research Library Reports

http://arq.lanl.gov/source/orgs/nmt/nmtdo/AQarchive/AQhome/AQissues.shtml - Seaborg Institute for Transactinium Science Publication Actinide Research Quarterly

http://www.osti.gov/bridge/ - Information Bridge: DOE Scientific and Technical Information

http://www.fas.org/sgp/othergov/doe/lanl/ - Los Alamos National Laboratory Reports

http://www.fas.org/irp/agency/dod/jason/ - JASON Defense Advisory Panel Reports

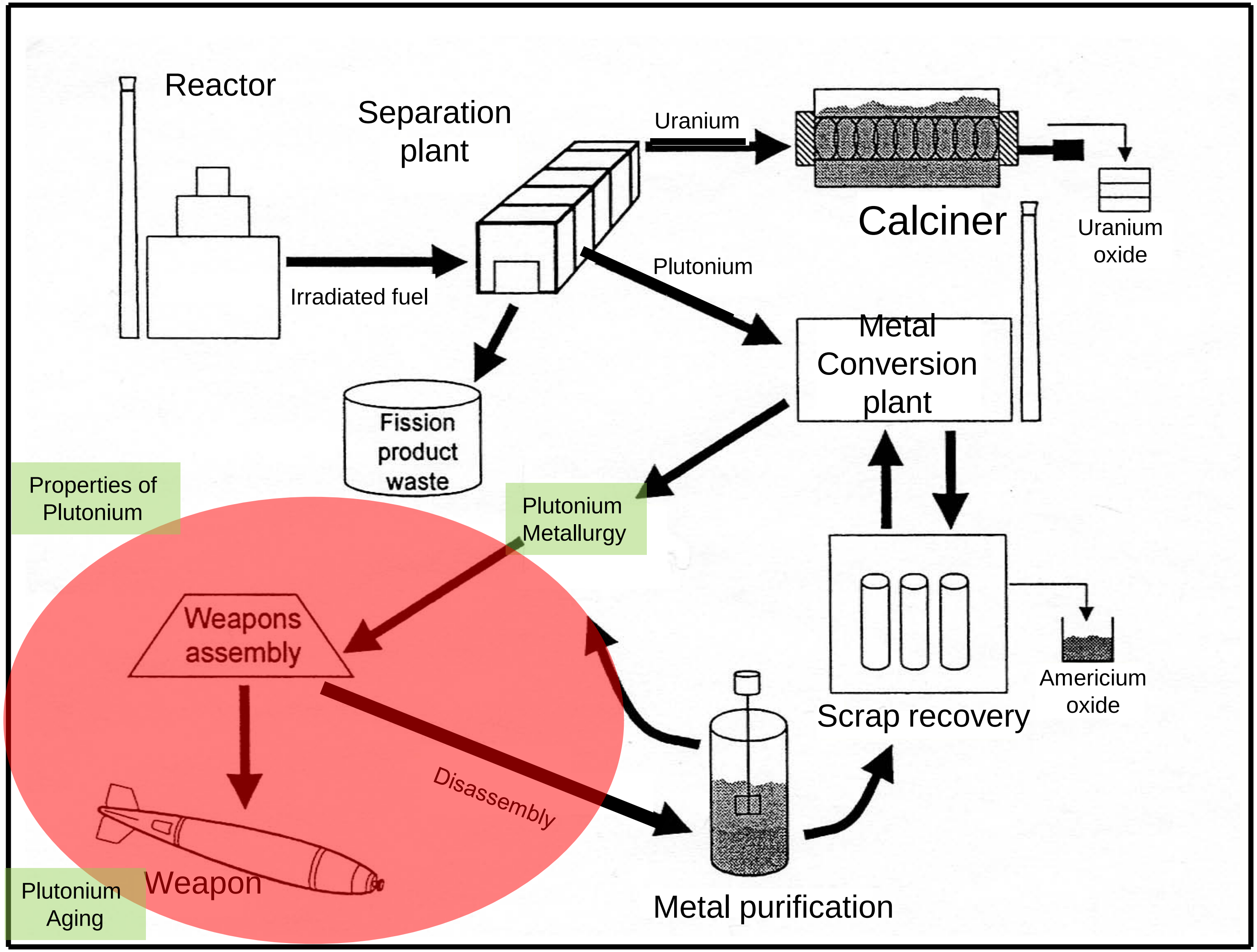
Plutonium: Materials Science and Technological Uses

Plutonium Applications

All stem from special nuclear properties of Pu

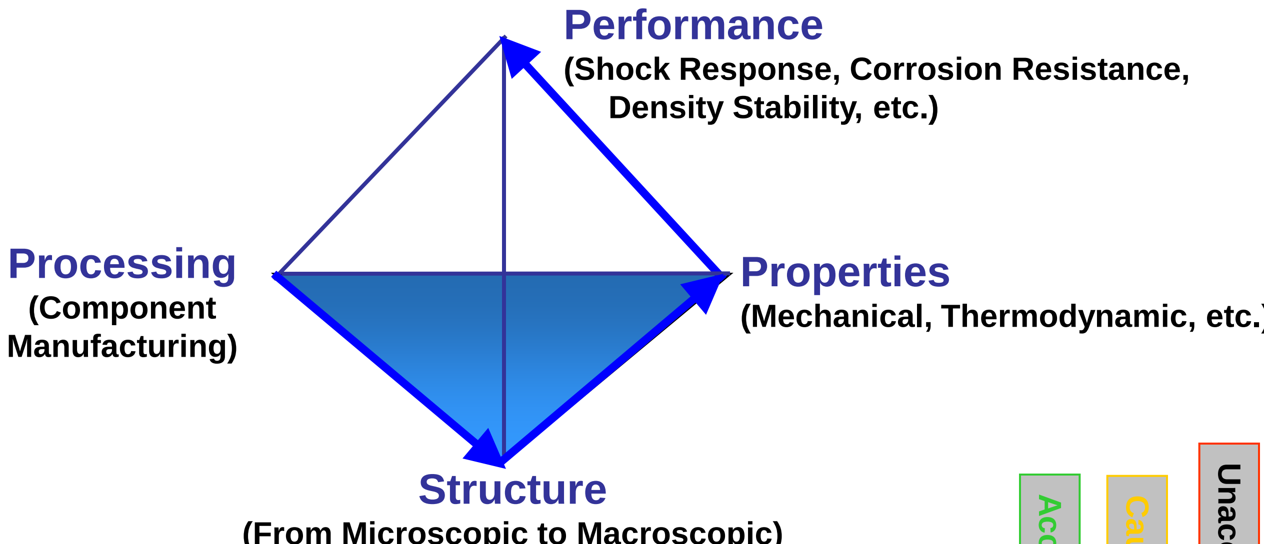
^{239}Pu Metal :	**Nuclear weapons** **Early nuclear reactors**
^{239}Pu Oxide :	**Nuclear reactors** **Mixed oxide fuels** **$^{238}UO_2$-20%$^{239}PuO_2$**
^{238}Pu Oxide :	**Radioisotope heat sources** **Fuel for space power systems**

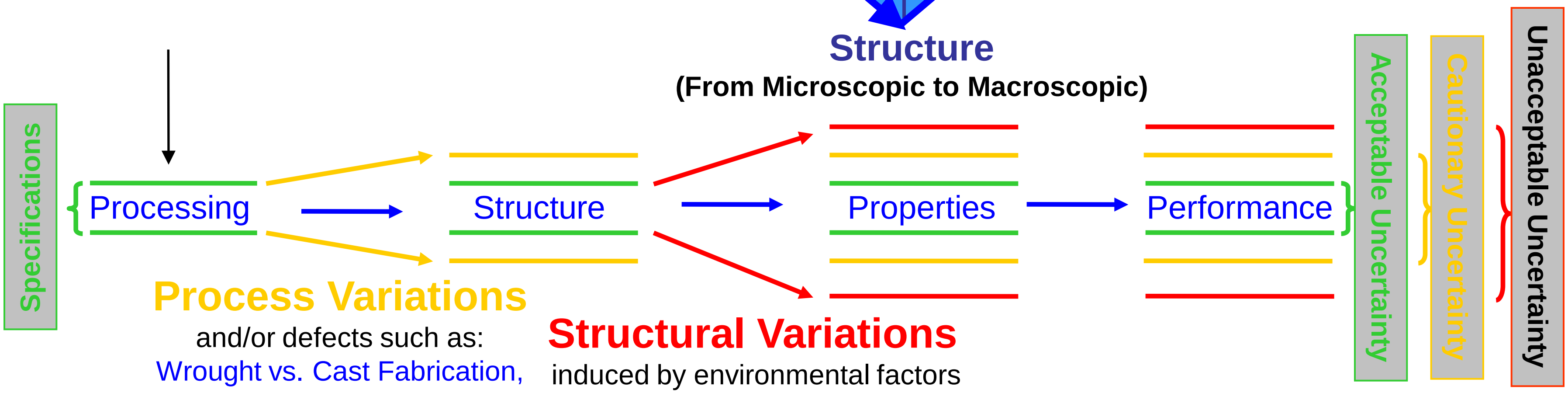
Plutonium Processing Cycle



Materials Science Tetrahedron Applied to Weapons Materials

<u>Established Manufacturing Process</u>
Known performance and margin based on well-known causal relationship between processing specifications and resultant structure, properties, and performance.



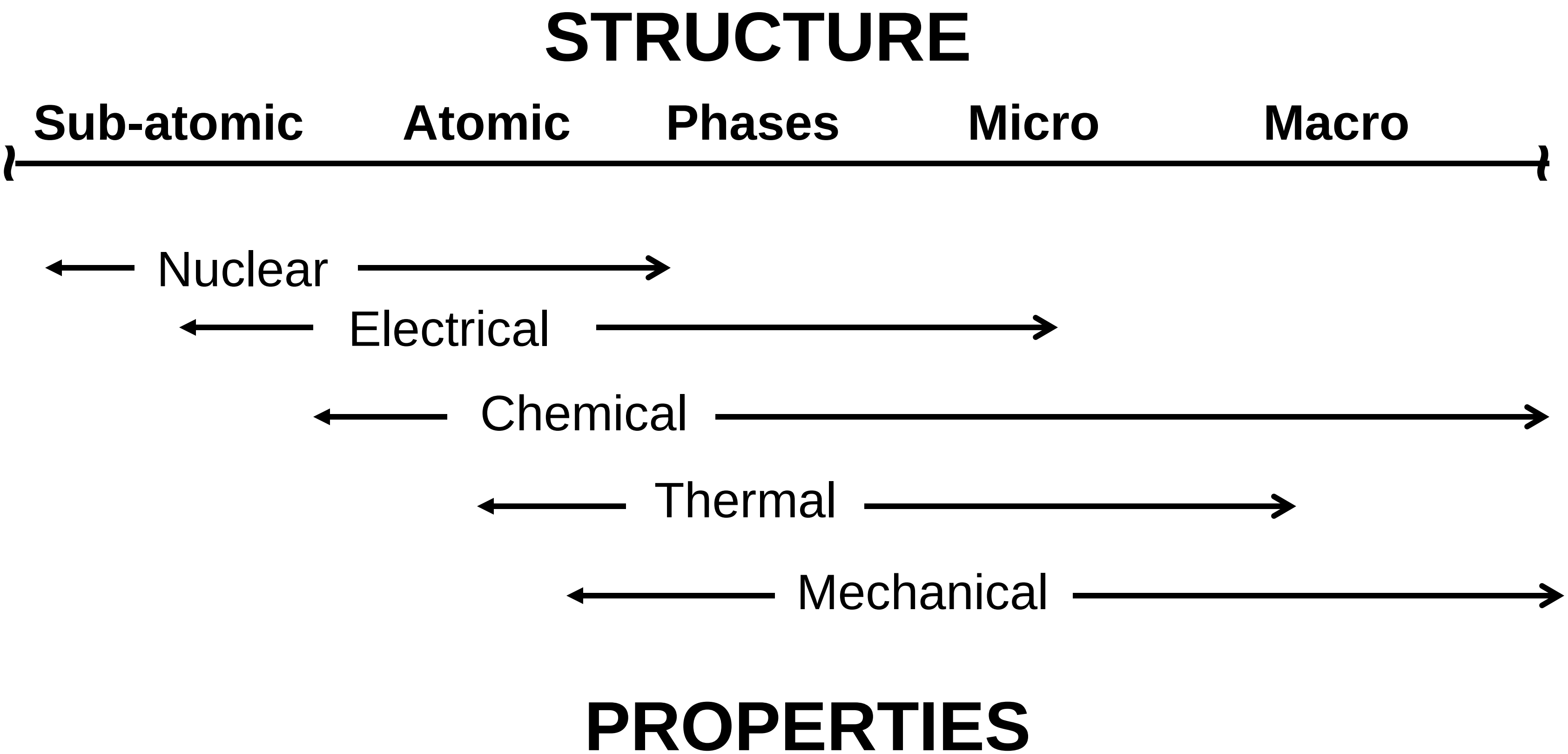


Process Variations
and/or defects such as:
Wrought vs. Cast Fabrication,
Casting Asymmetries and/or
Impurities and Inclusions
lead to structural variations.

Structural Variations
induced by environmental factors and/or "aging" such as:
Alloy Instability,
Self-Irradiation Damage,
Oxidation and Corrosion,
Fatigue and Fracture
lead to properties variations.

Variations (intentional or not) propagate through these casual relationships and must be understood to effectively manage **impact** to **performance uncertainty**.

The General Relationship of Material Structure Size in Determining Various Properties



Liquid Nuclear Fuels Data

LA-2358
CHEMISTRY--GENERAL
(TID-4500, 15th Ed.)

LOS ALAMOS SCIENTIFIC LABORATORY
OF THE UNIVERSITY OF CALIFORNIA LOS ALAMOS NEW MEXICO

REPORT WRITTEN: May 1959

THE DENSITY OF LIQUID PLUTONIUM METAL

by

C. E. Olsen, T. A. Sandenaw, and C. C. Herrick

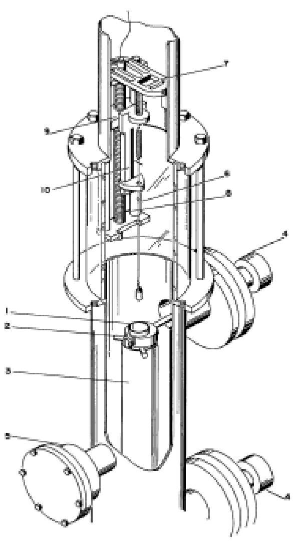


Fig. 1. Top of furnace and measuring apparatus.

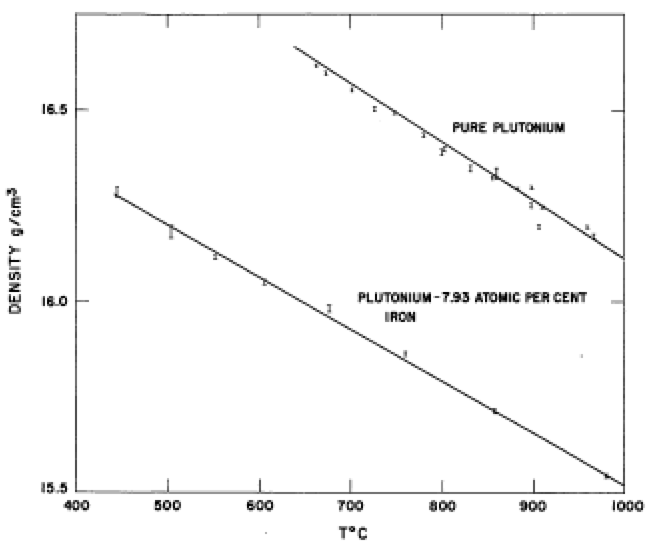


Fig. 2. Density vs temperature of plutonium-iron alloy.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 48, NUMBER 7 1 APRIL 1968

Fluid Flow of Liquid Plutonium Alloys in an Oscillating-Cup Viscosimeter

L. J. Wittenberg and D. Ofte*
Monsanto Research Corporation, Mound Laboratory,† Miamisburg, Ohio
AND
C. F. Curtiss
Theoretical Chemistry Institute, University of Wisconsin, Madison, Wisconsin
(Received 18 January 1967)

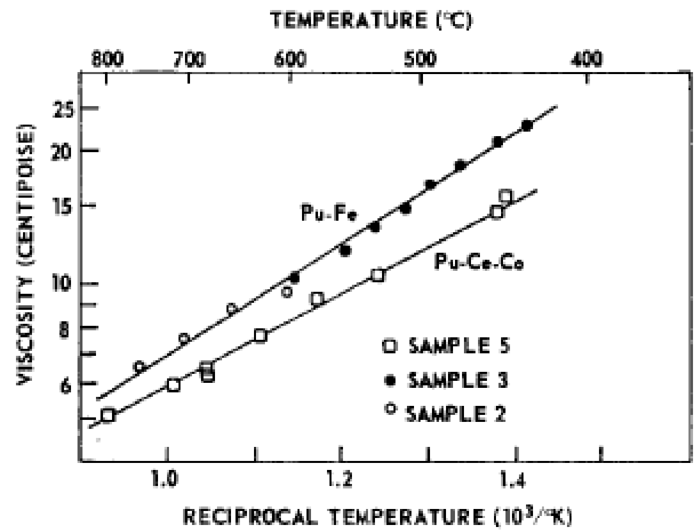


Fig. 6. Logarithm of viscosity as a function of reciprocal temperature for plutonium–iron and plutonium–cerium–cobalt alloys.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 56, NUMBER 9 1 MAY 1972

Volume Contraction During Melting; Emphasis on Lanthanide and Actinide Metals

LAYTON J. WITTENBERG AND ROBERT DEWITT
Mound Laboratory, Monsanto Research Corporation, Miamisburg, Ohio 45342*
(Received 4 November 1971)

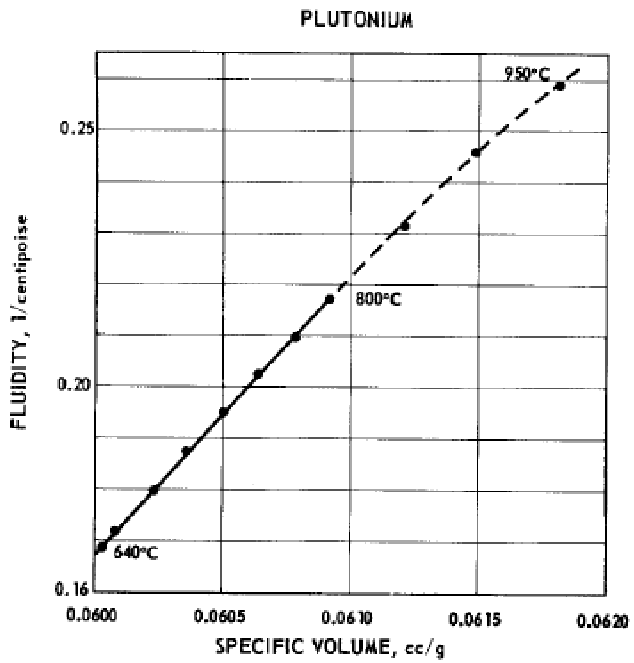


FIG. 2. Fluidity as a function of specific volume for liquid plutonium.

$$\eta^{-1}=(V_l-c)/B=(V_l/B)-(c/B).$$

$$\Delta V_f=(V_l-c)$$

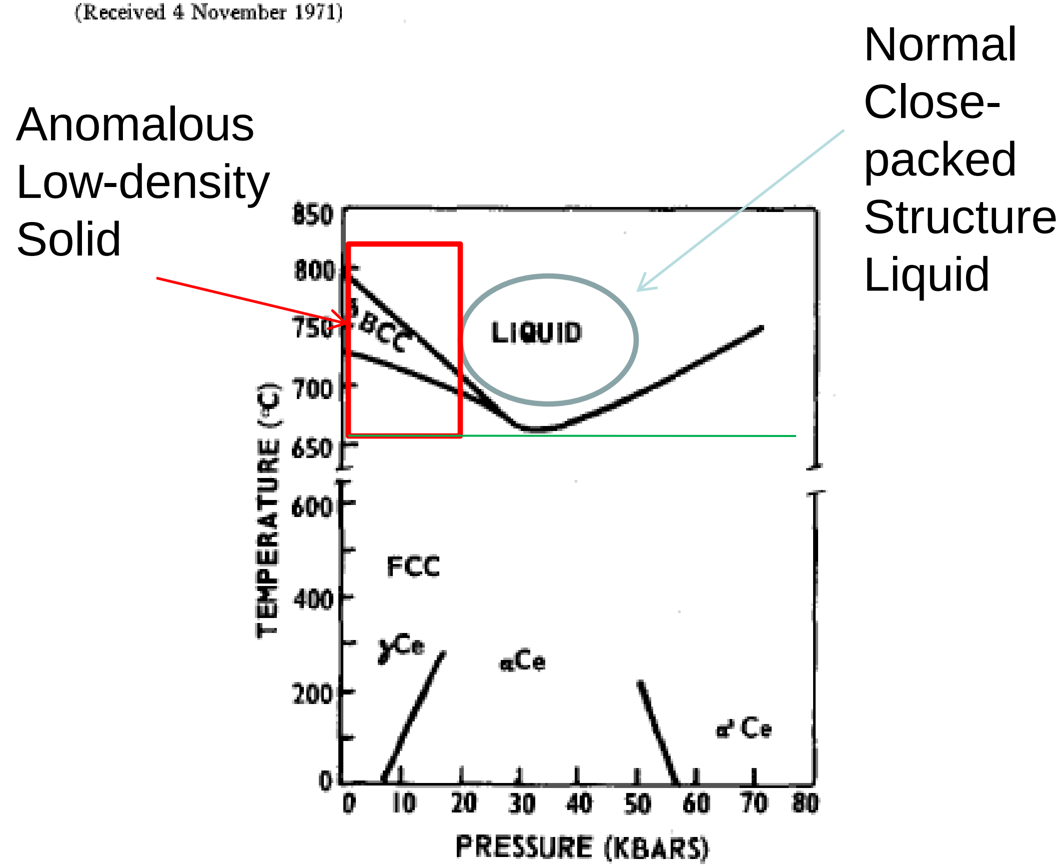


FIG. 6. Phase diagram of cerium (Ref. 16).

$$dT/dP=\Delta V_f/\Delta S.$$

UNCLASSIFIED

Plutonium Applications: MOX Fuels

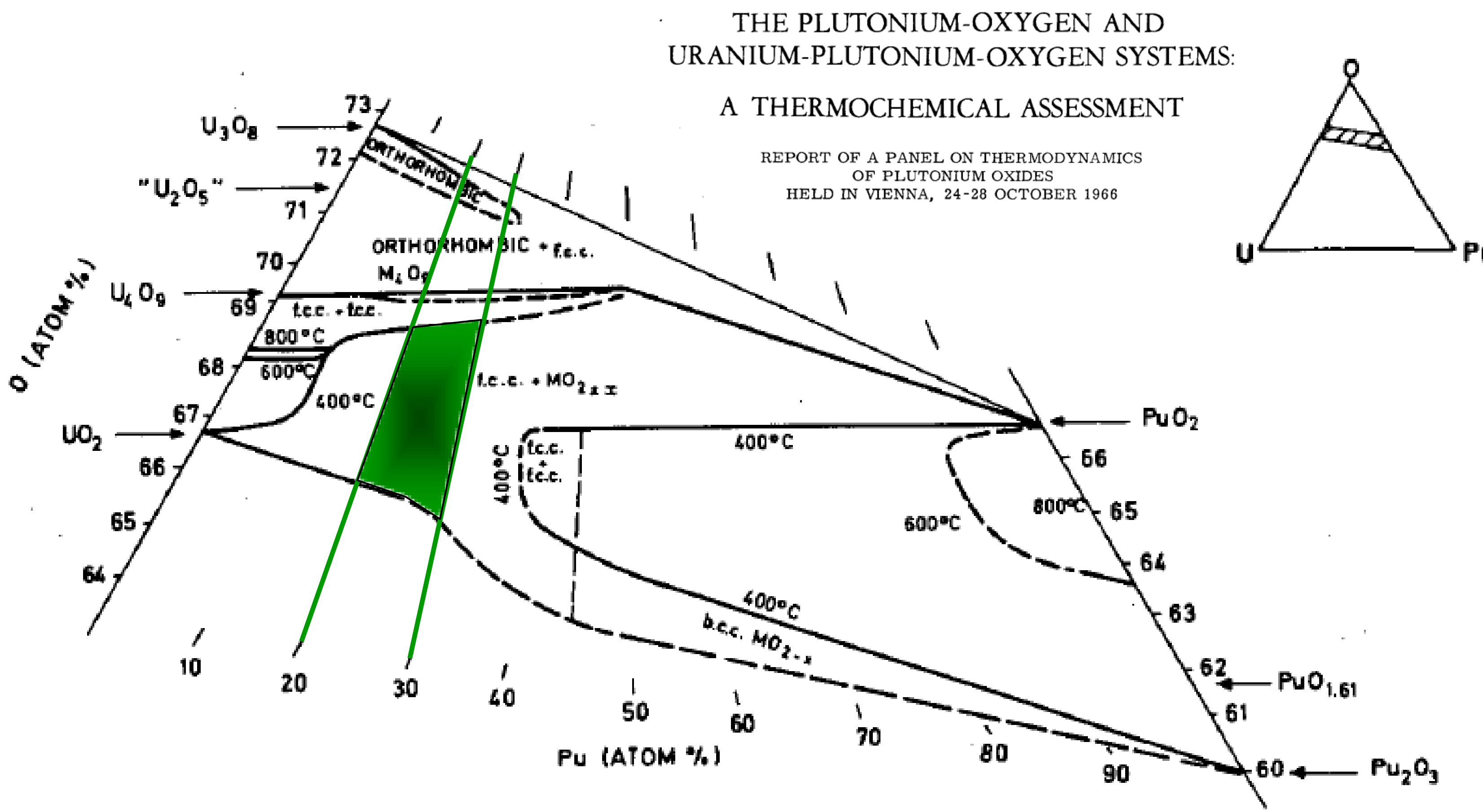
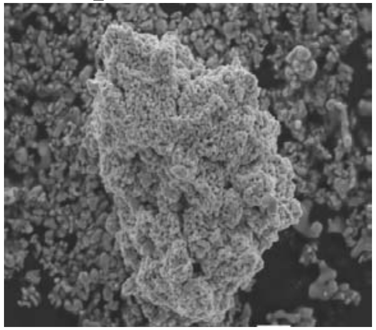


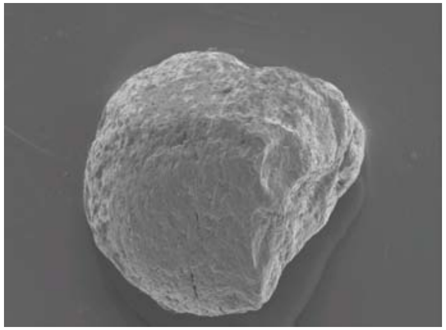
FIG. 13. U-Pu-O ternary section at 400, 600 and 800°C.

MAMOX: Precursor Oxide Particle Morphology and Fuels Microstructure

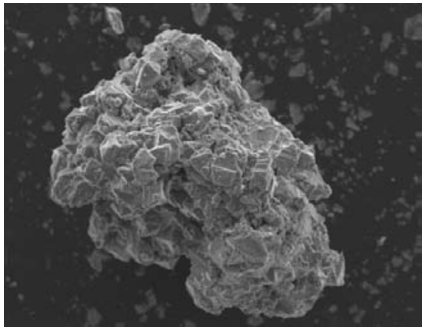
DUO_2 11,000x



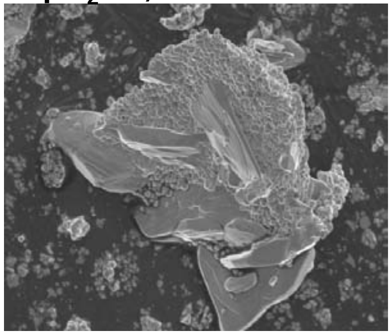
$HEUO_2$ 1,400x



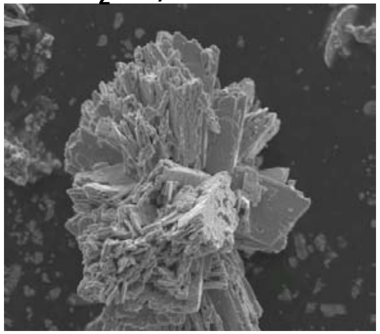
PuO_2 3,500x



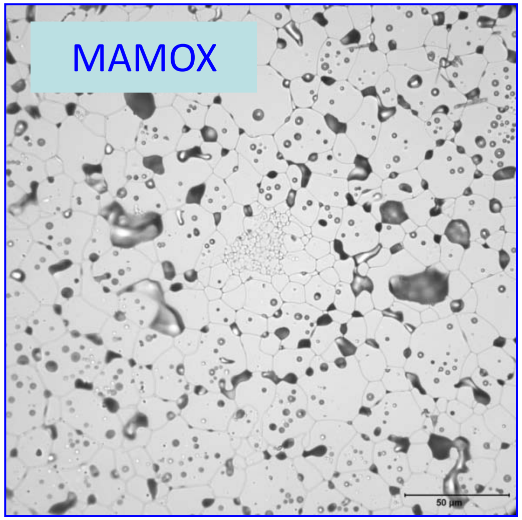
NpO_2 2,300x



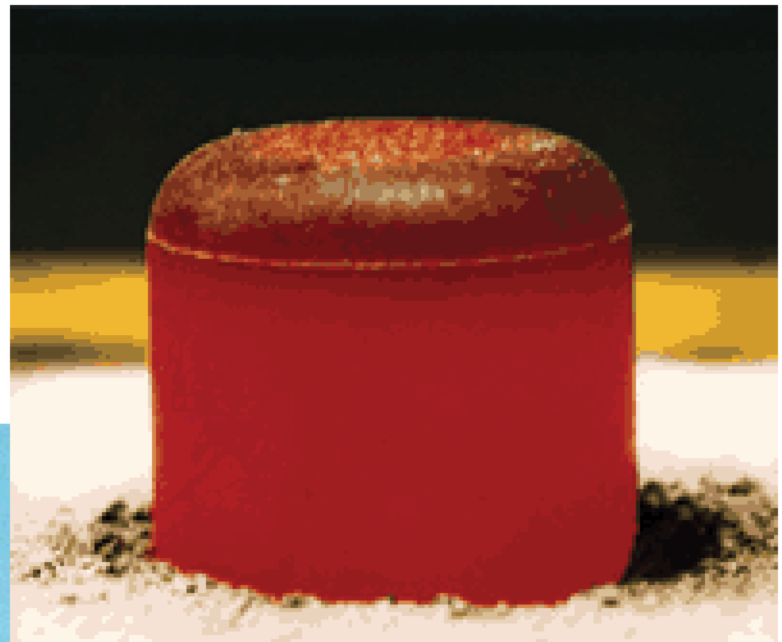
AmO_2 4,000x

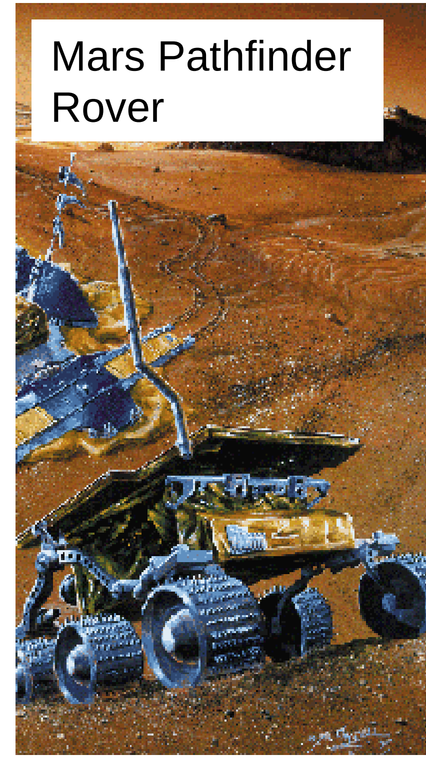


Pressing and Sintering



Encapsulation of Pu^{238} Oxide Heat Sources for NASA space missions





Radioisotope Thermoelectric Generator

Pu^{238} Oxide Energy Output: 0.54 watts/gram

Heat Source + Thermocouple = Electricity

Sebeck Effect: $\Delta V = \alpha \Delta T$

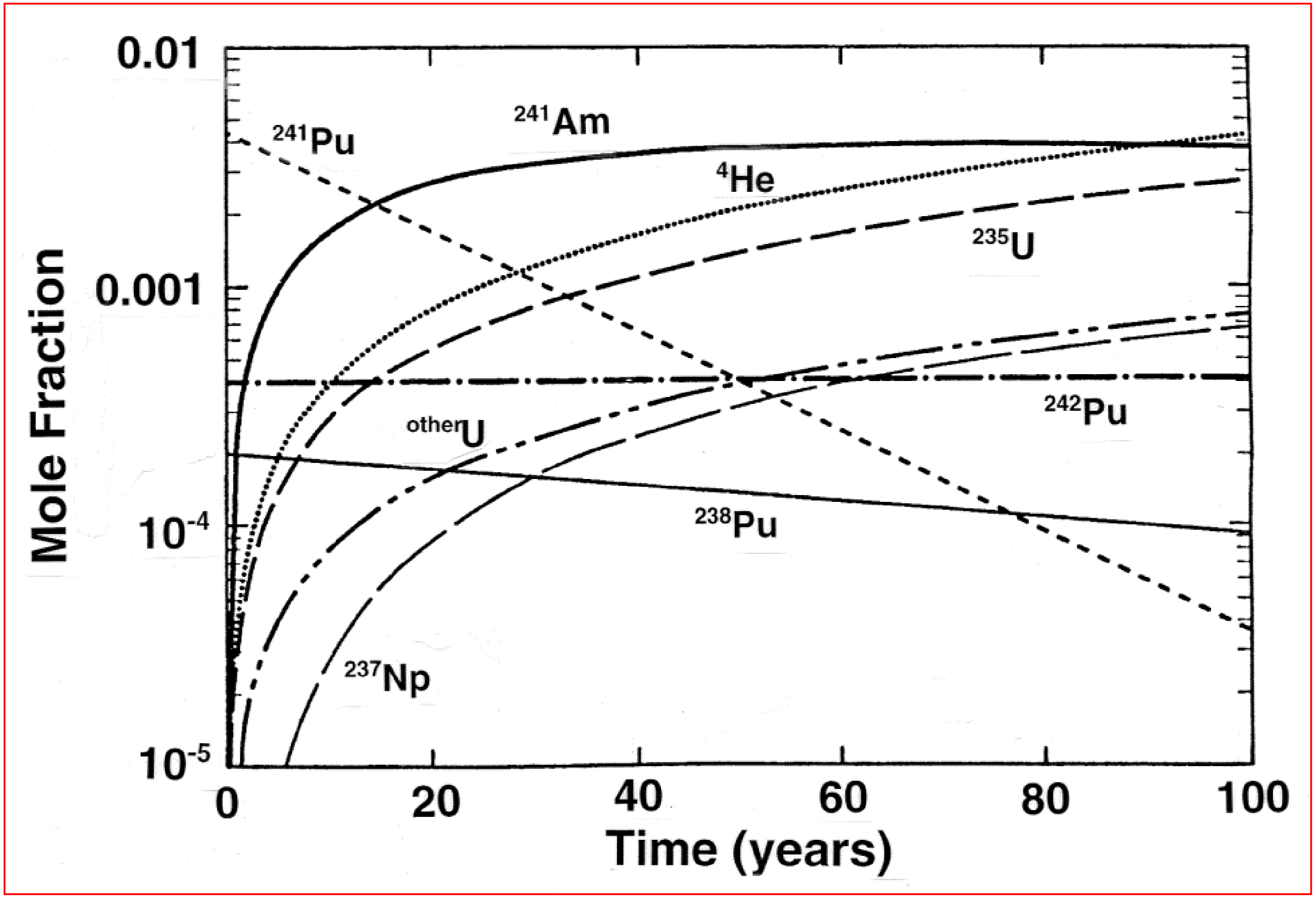
Pu Self-Irradiation and Induced Aging Effects

Plutonium Isotopes, Half-Lives and Typical Materials

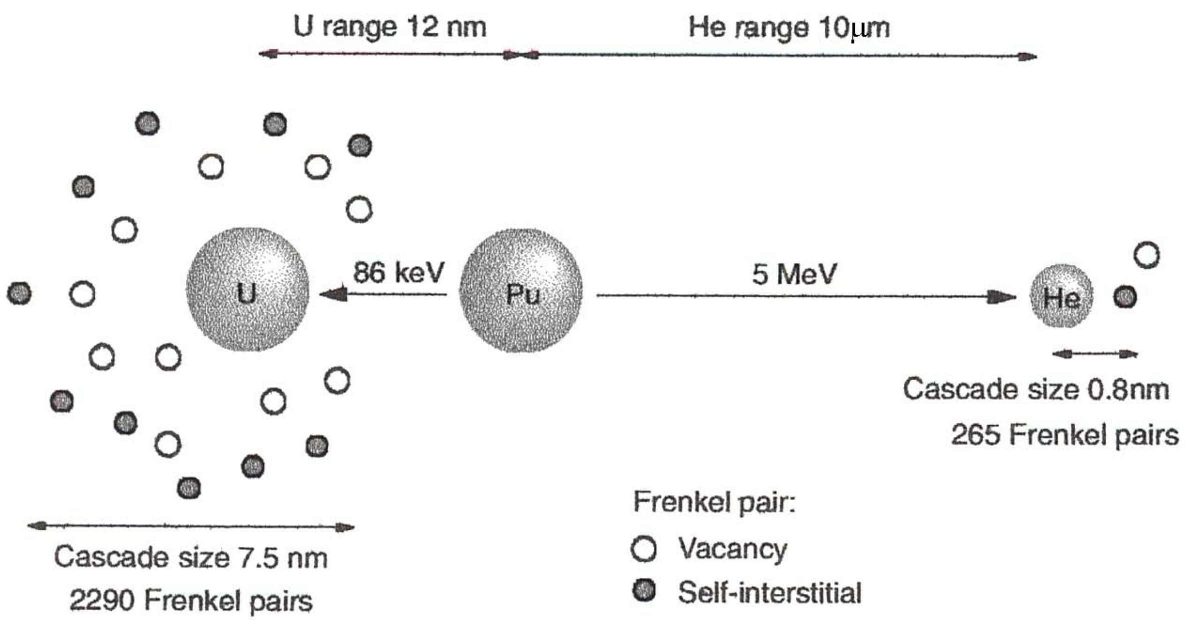
Isotope Mass #	$T_{1/2}$ Half-life	Thermal neutron fission	Weapons Grade Plutonium (%)	Accelerated Aging (%)	Reactor Grade Plutonium (%)	Heat Source (%)
Pu^{238}	87.7 yrs	Probably	<0.05	7.5	1.5	90.0
Pu^{239}	24,100 yrs	Yes	86.1	93.6	58.1	9.1
Pu^{240}	6,560 yrs	No	6	6	24.1	0.6
Pu^{241}	14.4 yrs	Yes	0.4	0.4	11.4	0.03
Pu^{242}	3.8×10^5 yrs	No	<0.05	<0.05	4.9	<0.01
Pu^{244}	8.0×10^7 yrs	No	-	-	-	-

From: Nuclides and Isotopes, 14th ed., General Electric Co., San Jose, CA, 1989.

Daughter Product Ingrowth in Weapons Grade Pu



Radioactive Decay of Plutonium



Uranium: Energy Deposition: Significant (85keV into 72,000 Unit Cells ~ 1.2meV/Å^3)
Residual Defect Structures: vacancies and interstitials
Inclusion Phases?: U complexes, Solute-Solvent Complexes (δ-phase alloys)

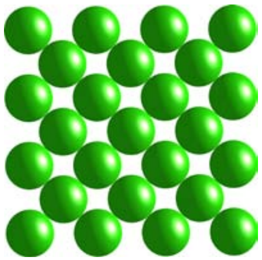
Alpha Particle: Energy Deposition: Minimal (5Mev into 40x10^{12} Unit Cells ~ 1.3neV/Å^3);
Residual Defect Structures: not likely
Inclusion Phases: He Bubbles

Perspective: Atoms to Bulk

Relative Dimensions		**Type of Defect**
0.5 - 3 Å	Atom	**Electron** **p^+, n^-**
3^+ - 5 Å	Unit Cell	**Point** **Vacancy**
10's - ~10^4 Å	Grains	**Line & Plane** **Dislocations,** **Faults,** **Boundaries**
10^2 Å - very large	Bulk	**Volume** **Voids,** **Bubbles,** **Inclusions**
	Process	**Flaws, "Cracks"**

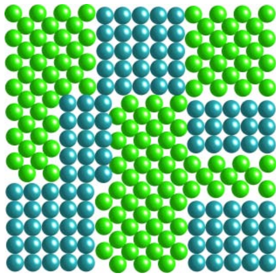
Plutonium Aging: Length Scales and Properties

Atomic scale ~ 10 Å



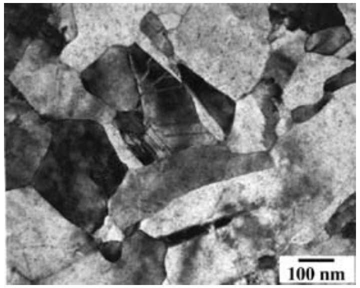
atomic structure

Nanoscale ~ 100Å



nano structure

Microscale ~ 100μ



bulk properties

Macroscale ~ 100cm

component processes

Fundamental structure of homogeneous materials

- Ga Distribution
- Impurities/Inclusions
- Lattice Constants
- Local Micro-structure
- Defect Structure
- Self-irradiation Damage
- Phase Stability
- Ga, Pu diffusion

Bulk properties of average structures, and heterogeneous materials

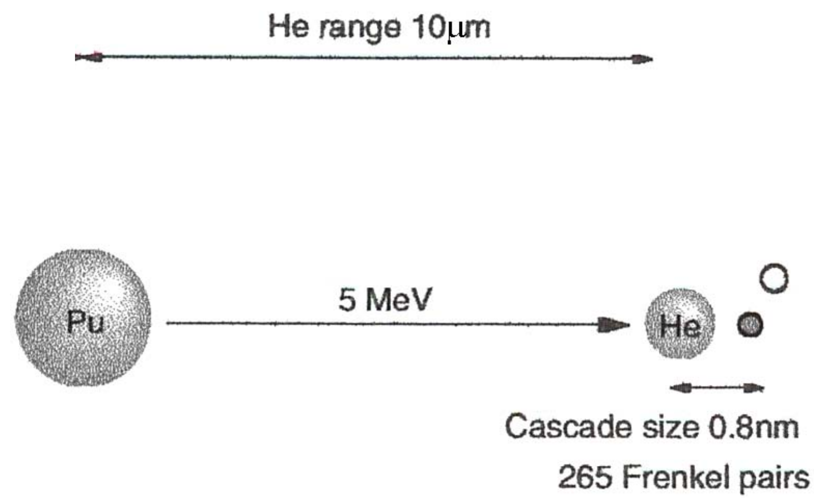
- lattice damage
- void swelling / He ingrowth
- He bubble formation
- Ga distribution "Coring"
- elastic properties
- density changes
- grain size
- dislocation structure

Controlling effects of heterogeneities, process coupling (chem, phys, mech)

- mechanical behavior
- dynamic properties
- stress-strain response
- strength, embrittlement
- weld stability
- corrosion behavior
- spall strength
- dimensional stability

Effects of Alpha Particle Decay Branch

Nanoscale:
- Atomic He insoluble → He atoms coalesce → bubble nucleation and formation; and
- Local heating/damage from U-decay maintains some He in solution.



Microscale:
- Bubbles coalesce at grain boundaries (denuded region); and
- Nonequilibrium bubble growth and coalescence at temperatures greater than 500K.

Macroscale:
- Linear volume swelling with age;
- Volumetric expansion with bubble growth and coalescence ; and
- Bubbles introduce changes in thermophysical properties.

Helium Bubbles in Aged δ-Pu Plutonium

Characterization and modelling of helium bubbles in self-irradiated plutonium alloys

A. J. SCHWARTZ*†, M. A. WALL†, T. G. ZOCCO‡ and W. G. WOLFER†

†Lawrence Livermore National Laboratory, Livermore, CA 94550, USA
‡Los Alamos National Laboratory, Los Alamos, NM 87545, USA

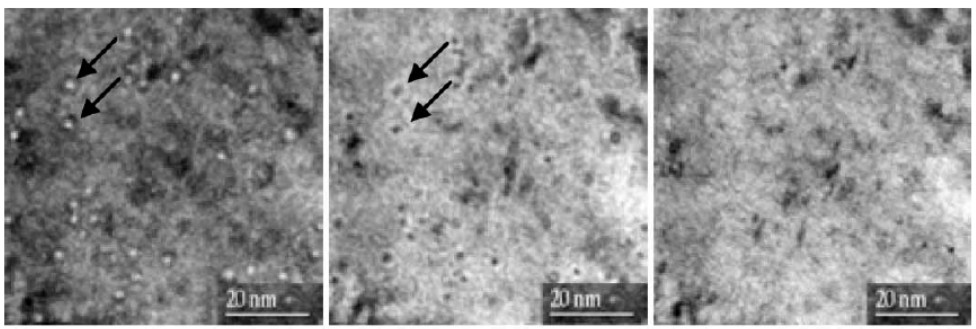


Figure 1. TEM images of 42-year-old Pu alloy. (a) The −1.4 µm under-focus bright-field TEM micrograph shows a high number density of very small helium bubbles as a dark fringe surrounding a light dot. (b) The + 1.4 µm over-focus image reveals the bubbles as light fringes surrounding a dark dot. (c) The in-focus image does not reveal the presence of bubbles due to the absence of a strain field.

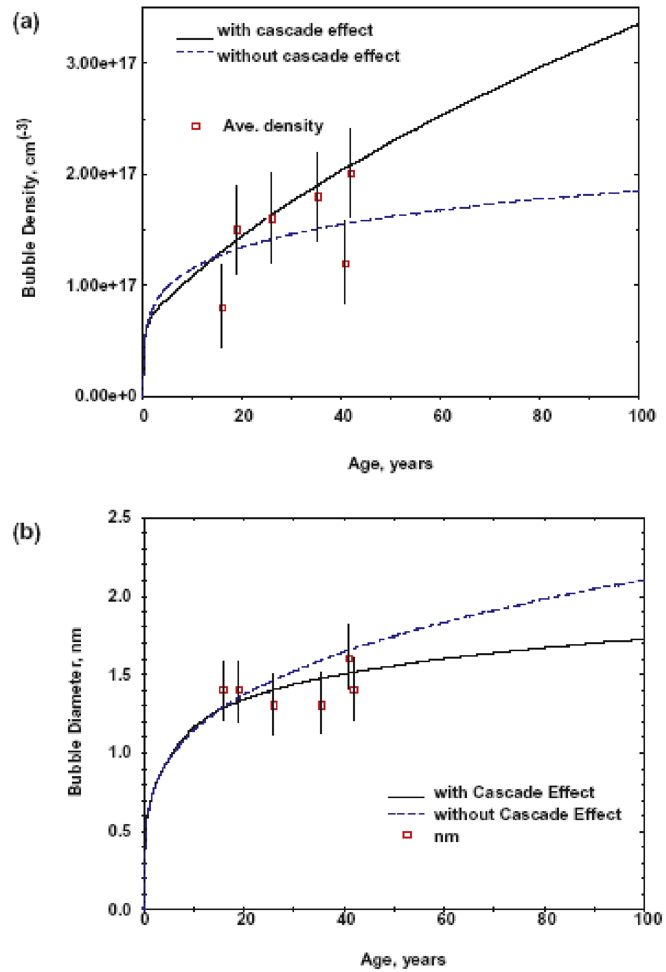
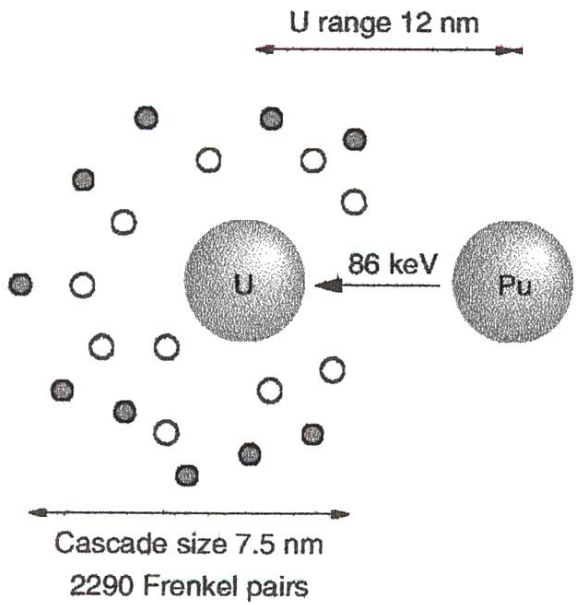


Figure 6. (a) Predicted helium bubble density and (b) average bubble diameter as a function of the plutonium age or the helium content (411 ppm He is generated in 10 years).

Effects of Uranium Decay Branch

<u>Nanoscale:</u>

- Local "defects" or local ordering;
- Defect concentration saturates to a value proportional to alloy solute concentration → defect structure likely involves solute atoms;
- Defect distorts/strains local lattice; and
- Local heating/damage from U-decay anneals out some defects.



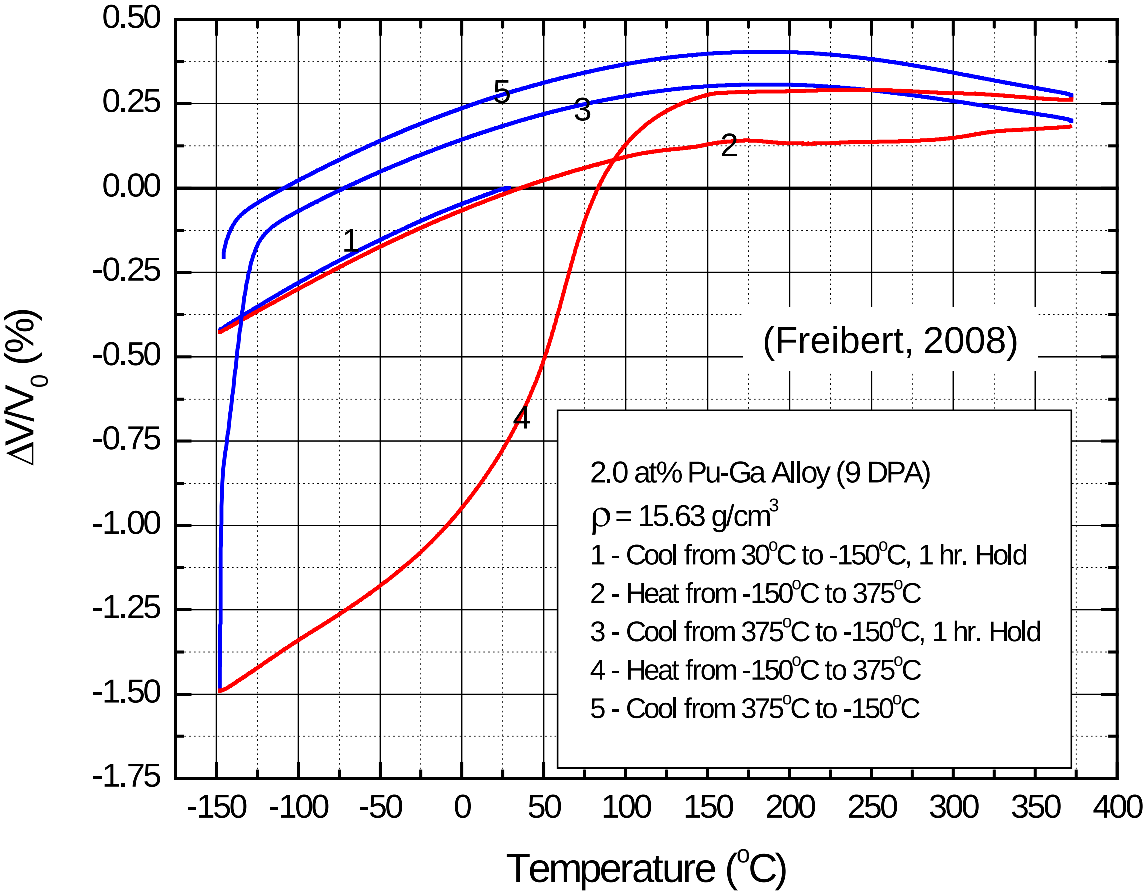
<u>Microscale:</u>

- Defects pin dislocations; and
- Defect generated strain field impedes δ→α' transformation.

<u>Macroscale:</u>

- Volume swelling from damage to point of saturation;
- Aging related mechanism increases yeild strength and removes strain rate dependence of flow stress; and
- Damage introduces transient changes in elastic moduli and other thermophysical properties.

Defects Strain Lattice and Suppress Martensite Transformed Volume: Thermal Expansion of 7.5% ^{238}Pu Alloy at 9 DPA (Equivalent 90 Yrs.)



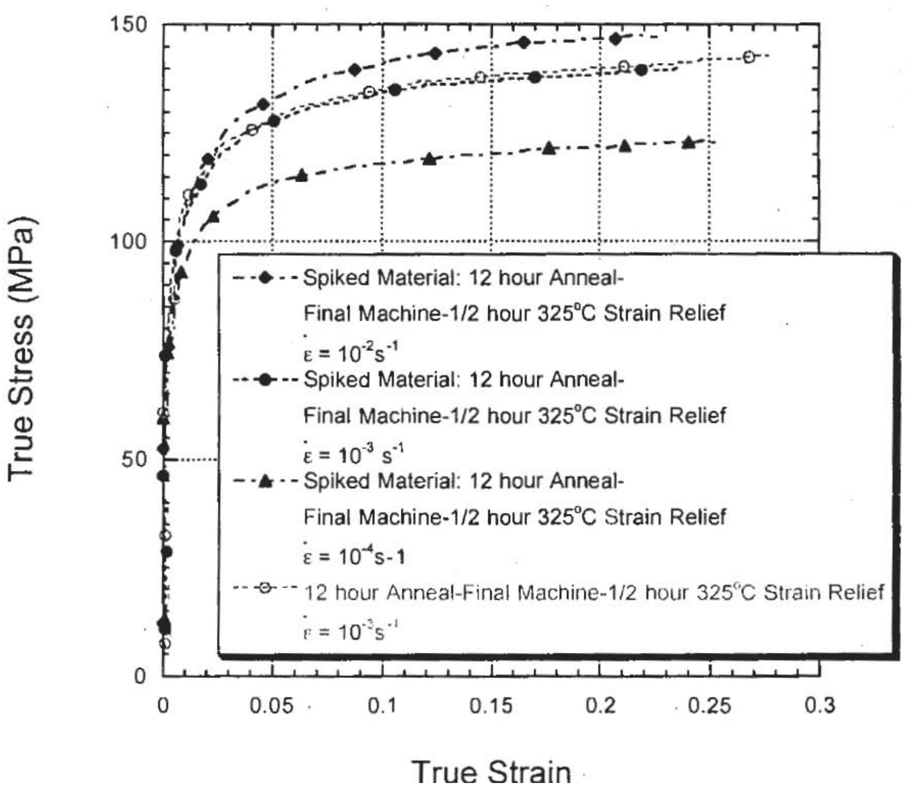
9DPA of accumulated self-irradiation damage totally suppresses the δ → α'.

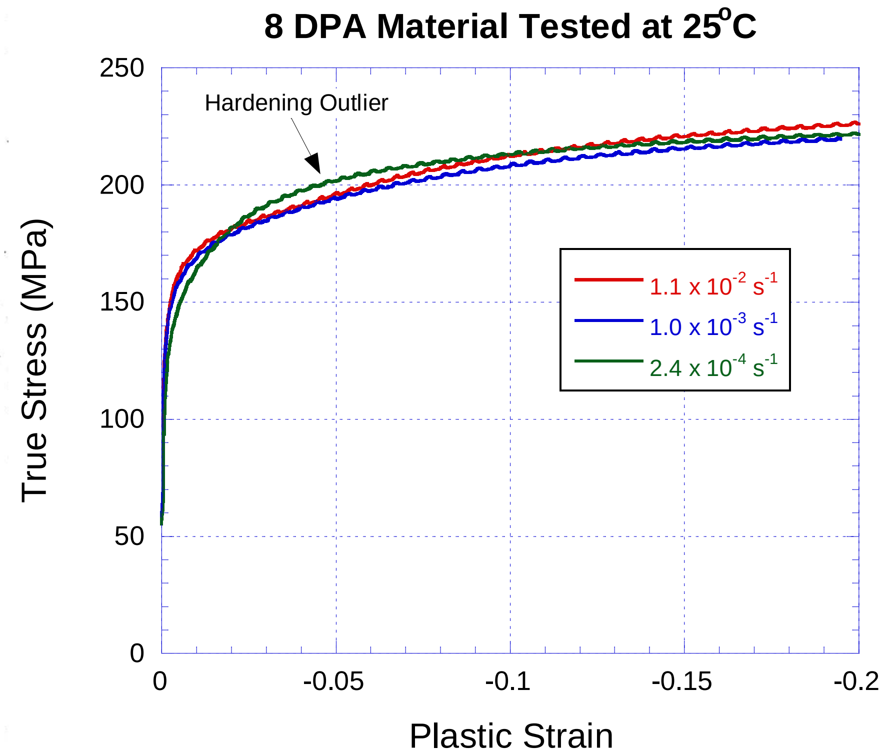
After damage anneals (T>150ºC), δ → α' occurs in agreement with 0.6 w/o Ga alloy (Hecker, 2001): Transformation Onset: -130 ^{0}C.

Full reversion (α' → δ) occurs from -150 to 150 ^{0}C.

Later thermal cycling shows:
- thermally induced swelling due to He bubble growth on heating; but
- typical δ-phase thermal expansion on cooling.

Self-Irradiation Damage Provides Strengthening Mechanism



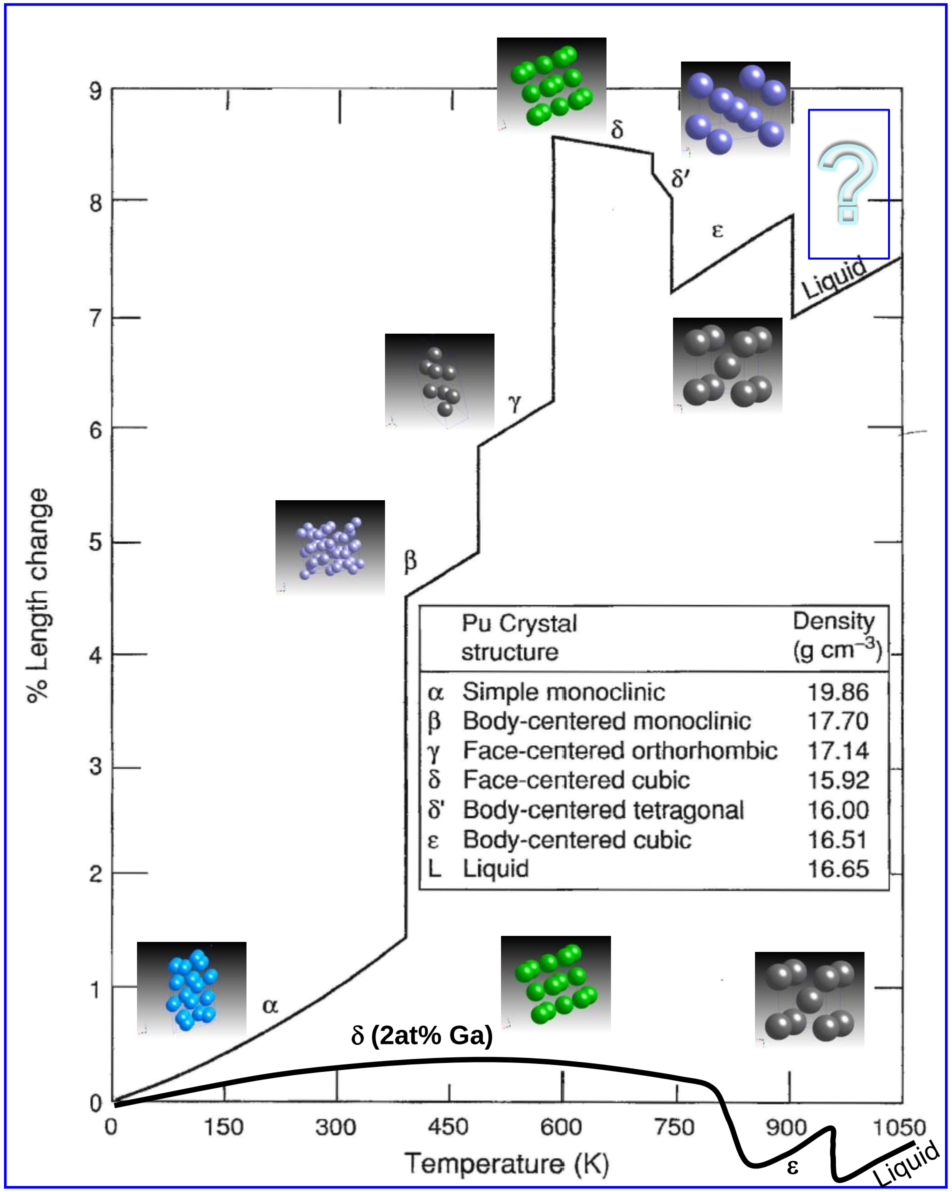


Damage (defects) likely acts to pin dislocations strengthening material under compressive load and dominating strain rate strength dependence. These data correlate with data from shear modulus changes (RUS) and micro-hardness measurements.

Unalloyed Plutonium Structural, Thermodynamic and Mechanical Properties

Crystal Structure Data for Plutonium

Phase	Stability Range °C	Space Lattice and Space Group	Unit Cell Dimensions, A	Atoms per unit Cell	X-ray Density, gm/cm³
α	Below ~115	Simple monoclinic *P*2_1/*m*	**@21 °C:** a= 6.183 ±0.001 b= 4.822 ±0.001 c= 10.963 ±0.001 β= 101.79° ±0.01°	16	19.86
β	~115-~200	Body-centered Monoclinic *I*2/*m*	**@190 °C:** a= 9.284 ±0.003 b= 10.463 ±0.004 c= 7.859 ±0.003 β= 92.13° ±0.03°	34	17.70
γ	~200-310	Face-centered orthorhombic *Fddd*	**@235 °C:** a= 3.159 ±0.001 b= 5.768 ±0.001 c= 10.162 ±0.002	8	17.14
δ	310-452	Face-centered cubic, *Fm*3*m*	**@320 °C:** a= 4.6371 ±0.004	4	15.92
δ'	452-480	Body-centered tetragonal *I*4/*mmm*	**@465 °C:** a= 3.34 ±0.01 c= 4.44 ±0.04	2	16.00
ε	480-640	Body-centered cubic, *Im*3*m*	**@490 °C:** a= 3.6361 ±0.004	2	16.51



Plutonium: An Inherently Unstable Element

- **Phase Transformations**
  5 Solid-Solid Allotropic Transformations
  Shear and Diffusion Driven
- **Thermodynamics**
  Quantitative and Qualitative Character
- **Kinetics (Heating vs. Cooling)**
  Rapid vs. Sluggish Atomic Movements
- **Ga as an Impurity**
  Interstitial (Lattice Const. increase: α')
- **Ga Alloying**
  Lowers δ-Pu Phase Free Energy and
  Stabilizes δ-Pu
  Substitutional in δ-Pu (XAFS)
  Alters Electronic Structure (TEC - → +)
  Diffusional δ↔ε transformation
- **Impact of Microstructure and Impurities**
  Grain size, Morphology, and Texture
  Pu_6Fe and other Inclusions
- **Anharmonic Effects**
  Non-Debye Solid Behavior

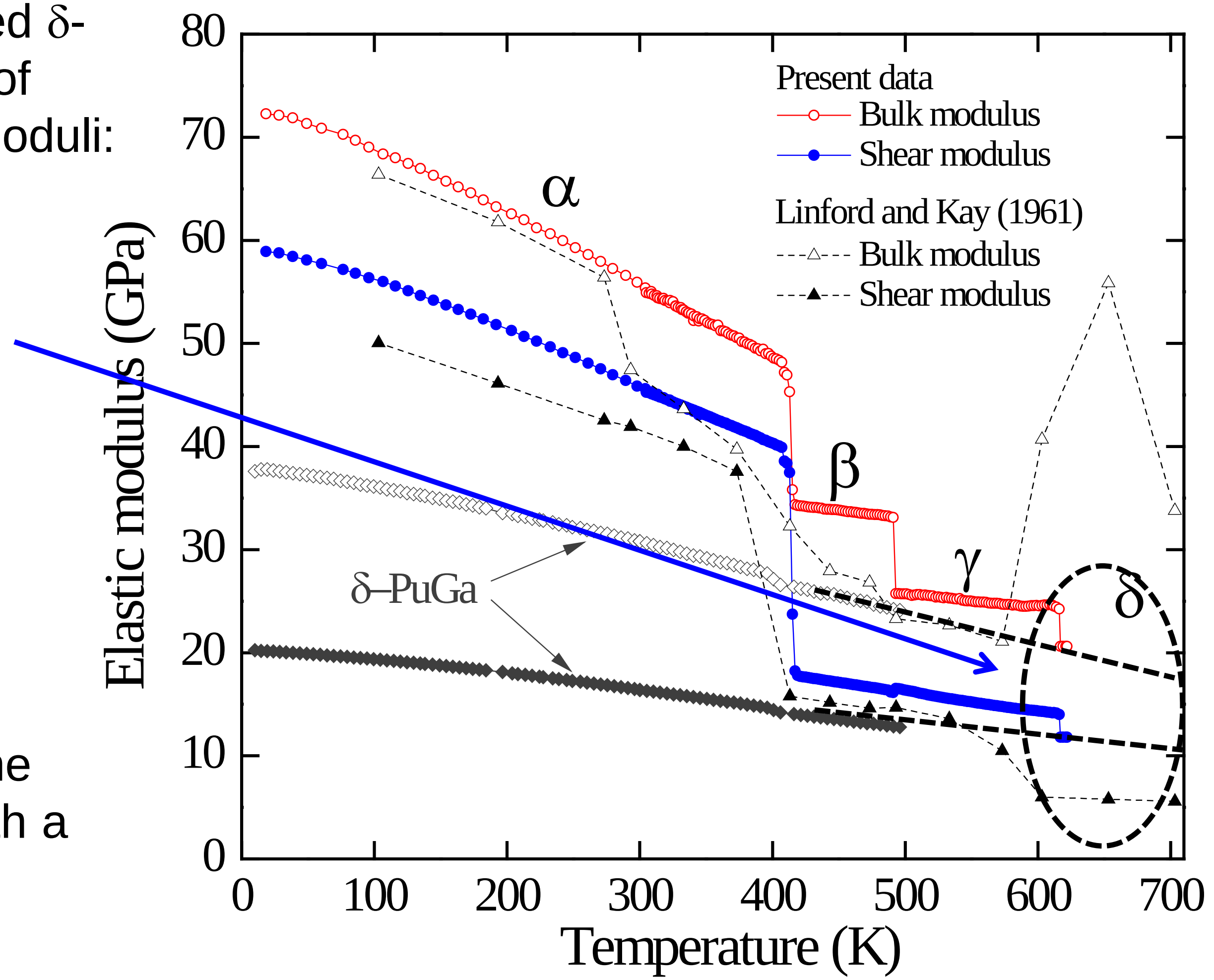
Unalloyed δ-Pu and 2at% Ga stabilized δ-Pu are elastically similar!

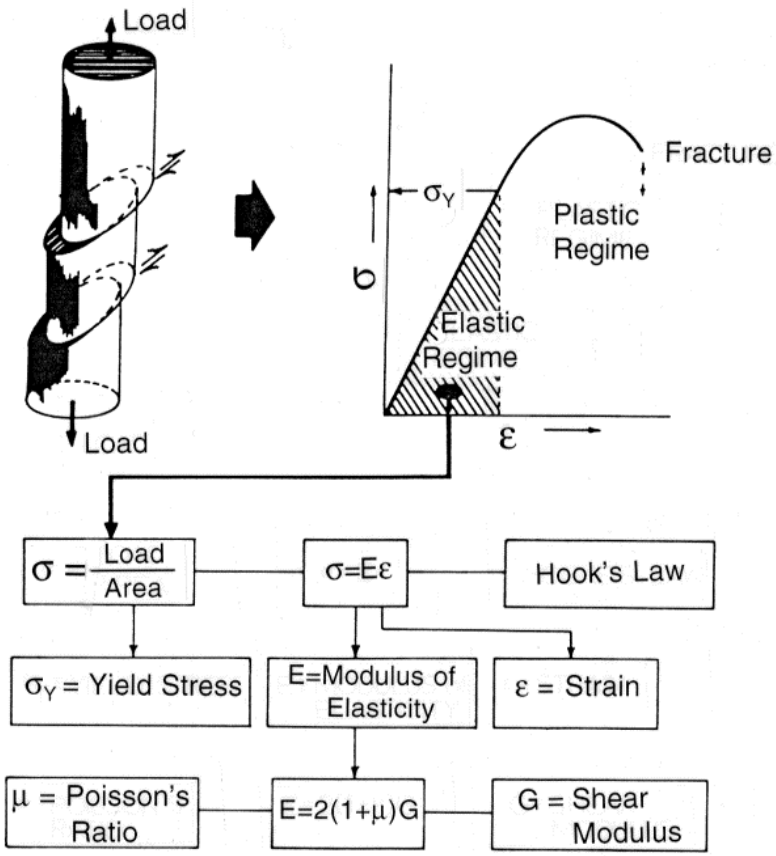
- Unalloyed and Ga alloyed δ-Pu exhibit same values of bulk and shear elastic moduli:

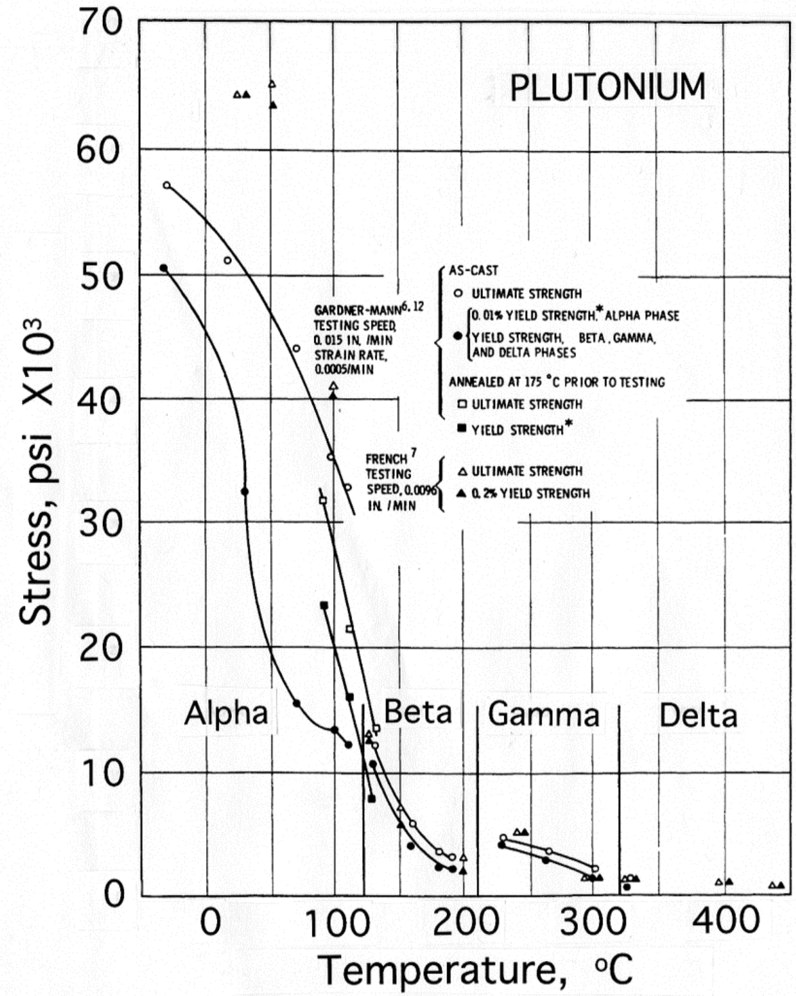
$$\left.\begin{aligned} B_{\delta-Pu} &= 20.6\ \text{GPa} \\ G_{\delta-Pu} &= 11.8\ \text{GPa} \\ B^{Ext.}_{\delta-PuGa} &= 22\ \text{GPa} \\ G^{Ext.}_{\delta-PuGa} &= 12\ \text{GPa} \end{aligned}\right\}$$

- α→β, β→γ, and γ→δ Pu transformation are continuous.

- β-Pu and γ-Pu exhibit the same shear modulus with a 30% variation in bulk modulus.




Load
Load
Fracture
σY
Plastic
Regime
σ
Elastic
Regime
ε
σ = Load / Area
σ=Eε
Hook's Law
σY = Yield Stress
E=Modulus of Elasticity
ε = Strain
μ = Poisson's Ratio
E=2(1+μ)G
G = Shear Modulus


PLUTONIUM
Stress, psi X10³
Temperature, °C
70
60
50
40
30
20
10
0
0
100
200
300
400
Alpha
Beta
Gamma
Delta
GARDNER-MANN6, 12
TESTING SPEED,
0.015 IN. /MIN
STRAIN RATE,
0.0005/MIN
AS-CAST
ULTIMATE STRENGTH
0.01% YIELD STRENGTH,* ALPHA PHASE
YIELD STRENGTH, BETA, GAMMA,
AND DELTA PHASES
ANNEALED AT 175 °C PRIOR TO TESTING
ULTIMATE STRENGTH
YIELD STRENGTH*
FRENCH 7
TESTING
SPEED, 0.0096
IN. /MIN
ULTIMATE STRENGTH
0.2% YIELD STRENGTH

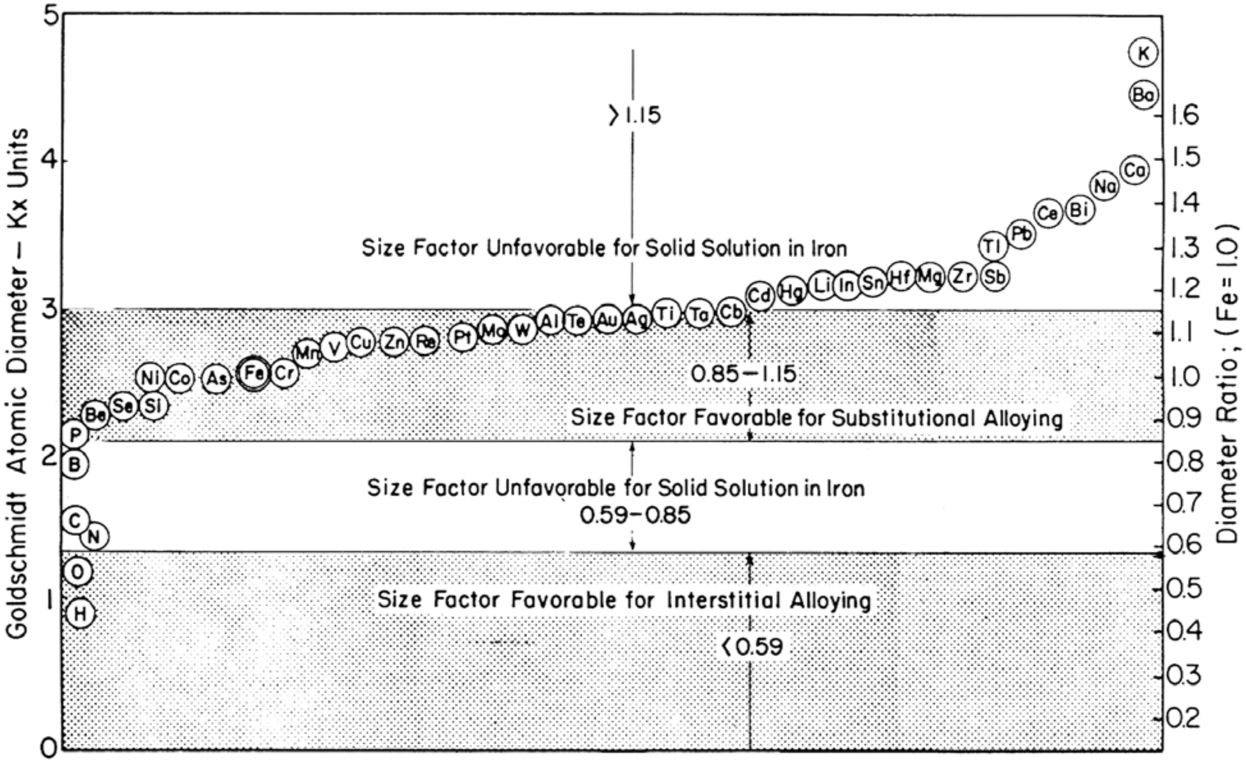
Plutonium Alloys and Metallurgy

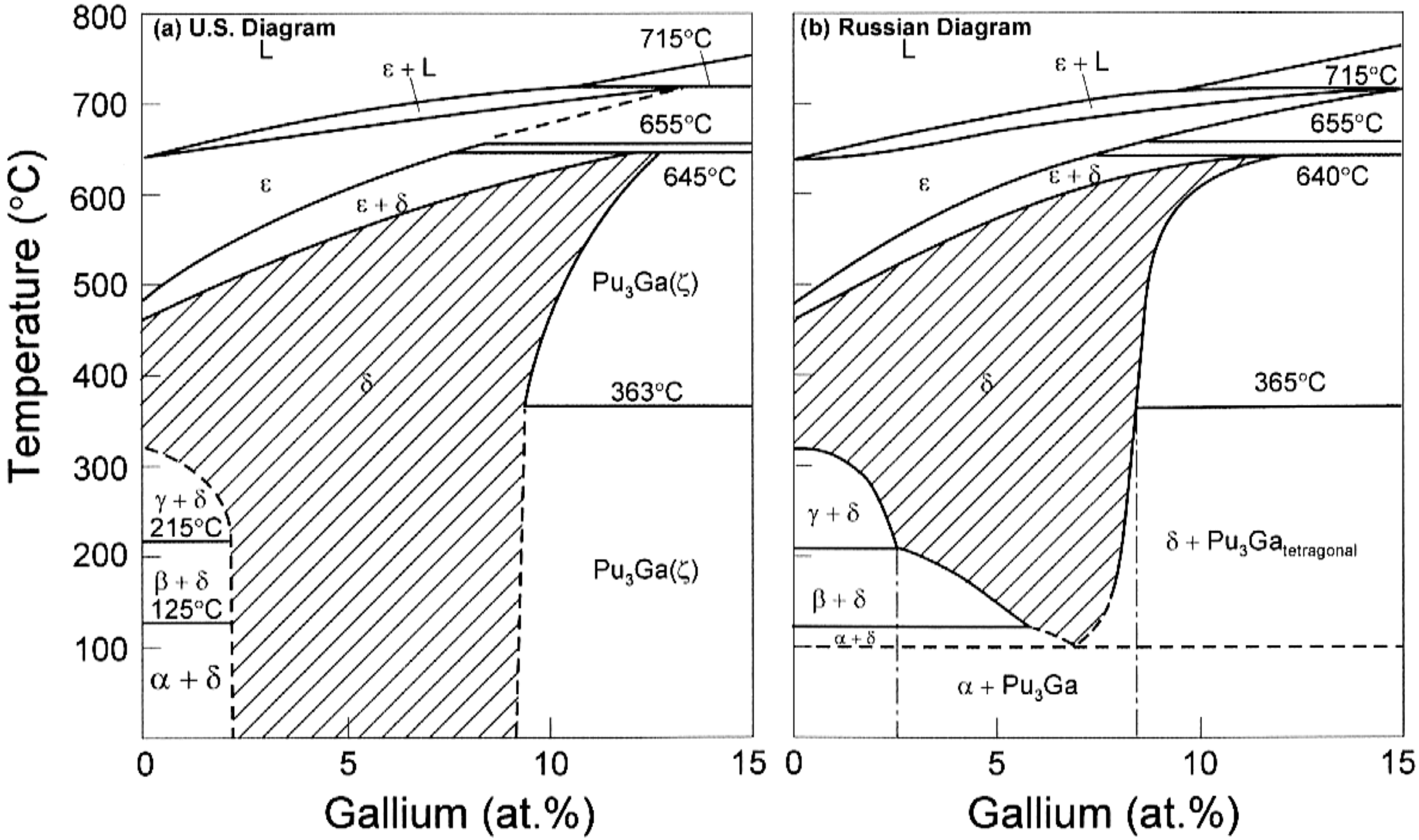
Elements that Alloy with Plutonium

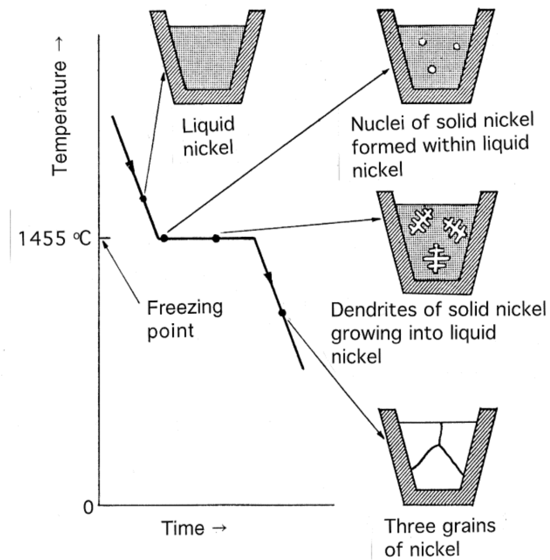
Phase		To R.T.	Not to R.T. (>1 wt. %)
α		Np, Ru, Zr	
β			Np, U, Zr
γ			Np, Th, U, Zr
δ		Al, Am, Ce, Ga, Sc	In, Np, Nd, Pm, Ru, Si, Sm, Th, Ti, U, Zn, Zr
δ′			Am, Np
ε			Ag, Al, Am, Ce, Cu, Dy, Er, Ga, Gd, Ho, In, Lu, Nd, Ni, Np, Os, Pd, Pm, Pr, Pt, Rh, Ru, Sc, Si, Sm, Th, Ti, Tm, U, Zn, Zr

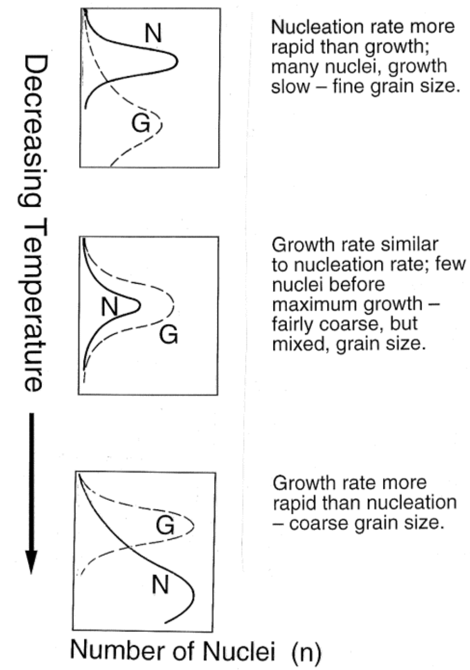
Hume-Rothery Rules for Complete Solid Solubility and Alloying

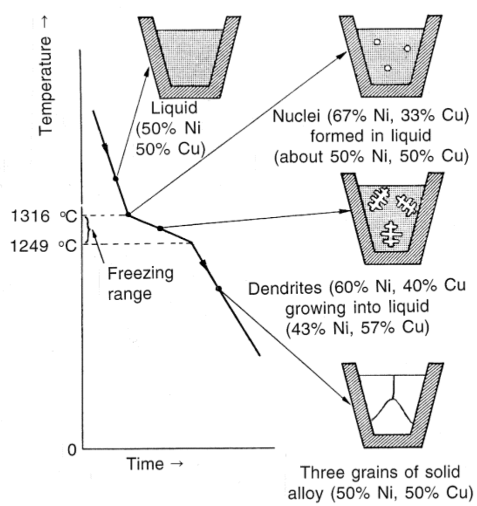
1. Must have the same crystal structure.
2. Less than ±15 % difference in atomic radii.
3. Same valence.
4. Similar electronegativity.

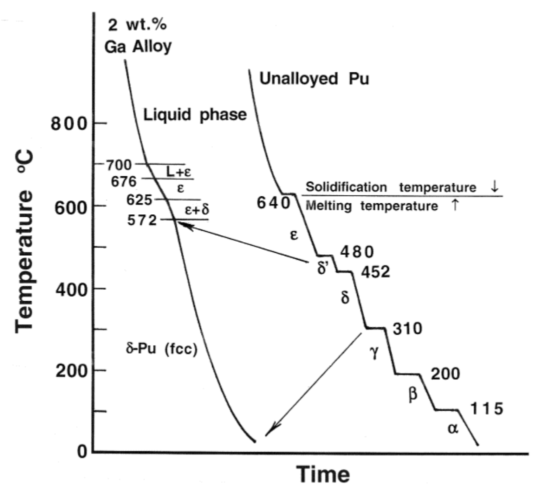


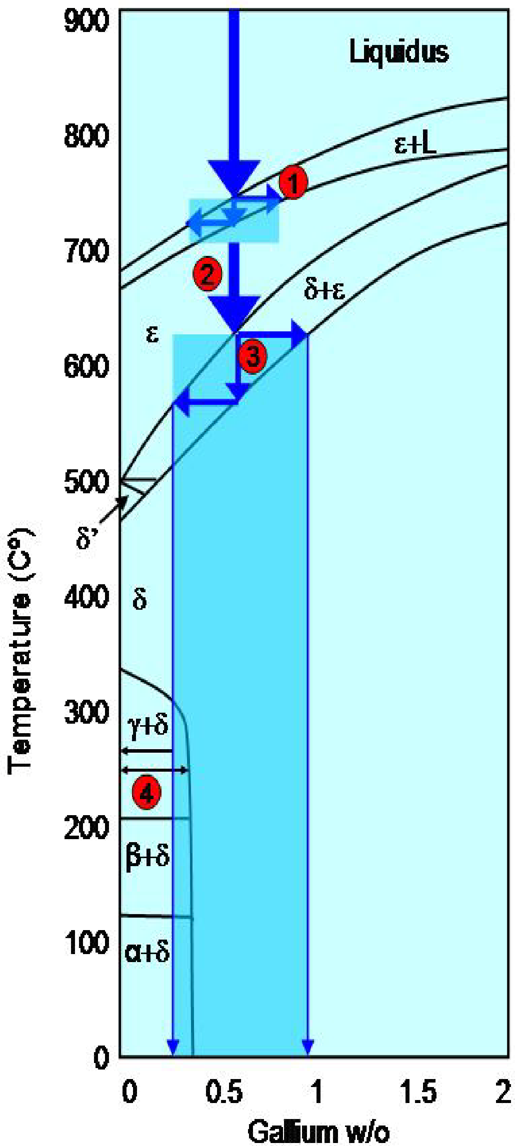

(a) U.S. Diagram
L
ε + L
715°C
655°C
645°C
ε
ε + δ
Pu3Ga(ζ)
δ
363°C
γ + δ
215°C
β + δ
125°C
Pu3Ga(ζ)
α + δ
(b) Russian Diagram
L
ε + L
715°C
655°C
640°C
ε
ε + δ
δ
365°C
γ + δ
δ + Pu3Ga tetragonal
β + δ
α + δ
α + Pu3Ga
Temperature (°C)
Gallium (at.%)
Gallium (at.%)
800
700
600
500
400
300
200
100
0
5
10
15


Temperature →
1455 °C
Freezing point
Liquid nickel
Nuclei of solid nickel formed within liquid nickel
Dendrites of solid nickel growing into liquid nickel
Three grains of nickel
0
Time →


Decreasing Temperature
N
G
Nucleation rate more rapid than growth; many nuclei, growth slow – fine grain size.
Growth rate similar to nucleation rate; few nuclei before maximum growth – fairly coarse, but mixed, grain size.
Growth rate more rapid than nucleation – coarse grain size.
Number of Nuclei (n)

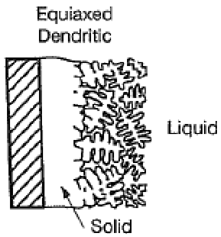

Temperature →
1316 °C
1249 °C
Freezing range
Liquid (50% Ni 50% Cu)
Nuclei (67% Ni, 33% Cu) formed in liquid (about 50% Ni, 50% Cu)
Dendrites (60% Ni, 40% Cu growing into liquid (43% Ni, 57% Cu)
Three grains of solid alloy (50% Ni, 50% Cu)
0
Time →


2 wt.% Ga Alloy
Unalloyed Pu
Liquid phase
Temperature °C
800
700
676
625
572
600
400
200
0
L+ε
ε
ε+δ
640
Solidification temperature ↓
Melting temperature ↑
ε
480
δ'
452
δ
310
γ
200
β
115
α
δ-Pu (fcc)
Time



Casting Pu-Ga Alloys

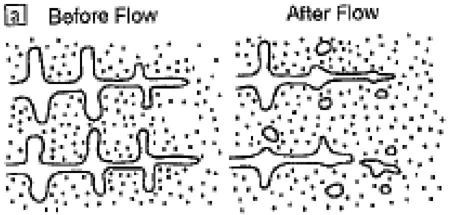
1



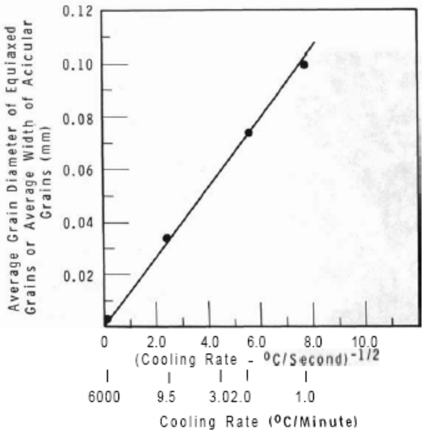
Solidification within ε+L phase field involves equiaxed dendrite formation initiated at the mold walls. Microsegregation of Ga or "coring" occurs.

2

Anisotropic negative thermal expansion and low yield strength in ε–phase results in plastic flow and dendrite breakage. Ga diffuses quickly due to high temperature and so reduces coring.



3



Microsegregation of Ga or "coring" occurs once again . Cooling rate through δ+ε phase field determines final cored grains.

4

Phase segregation occurs in Pu rich regions. Upon cooling, α-phase regions contain soluble Ga. Both α-phase and δ–phase regions remain metastable and under extreme residual stress due to density and thermal expansion differences of phases.

As-Cast Microstructure Shows Dark High-Gallium δ Cores Surrounded by Light Low-Gallium α Matrix

Theory

Modeling of Structural and Compositional Homogenization of Plutonium-1 Weight Percent Gallium Alloys

JEREMY N. MITCHELL, FRANK E. GIBBS, THOMAS G. ZOCCO, and RAMIRO A. PEREYRA

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Homogenization is dictated by Fick's Second Law:

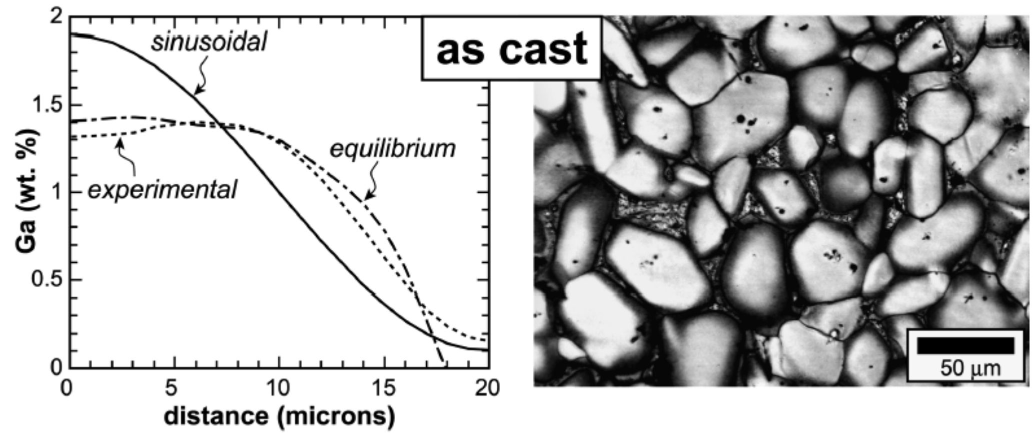
$$\frac{\partial C(x,t)}{\partial t} = D\frac{\partial^2 C(x,t)}{\partial x^2}$$

where D [cm^2/s] is the diffusivity

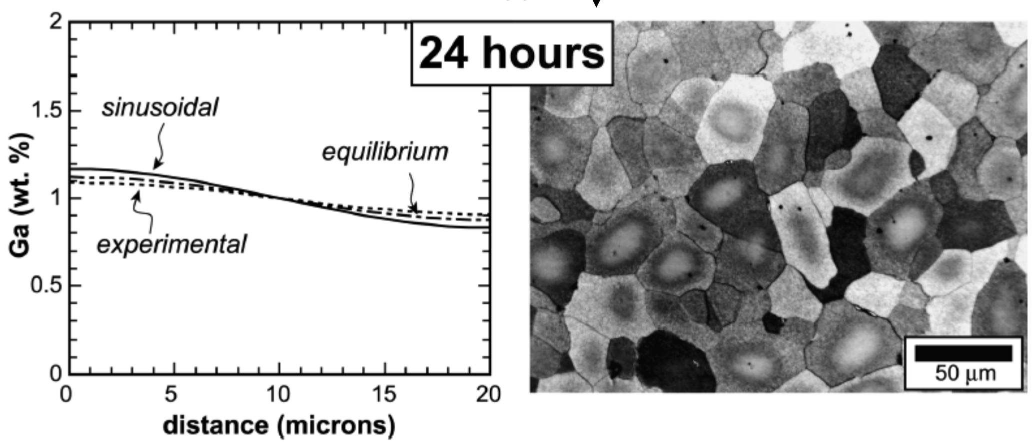
Diffusivity of Ga in Pu = ?

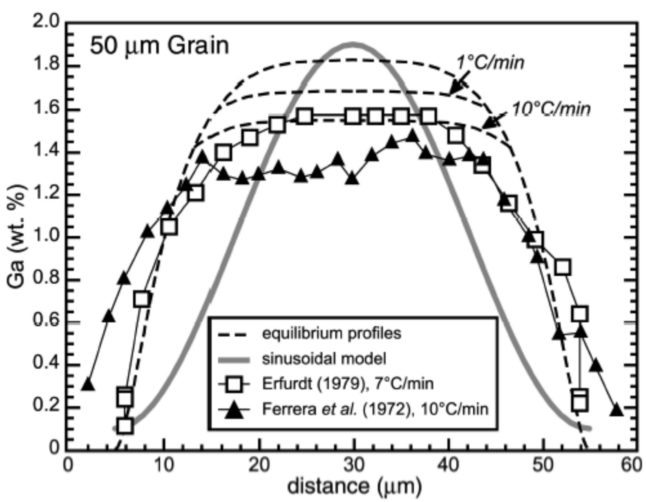
$$C(x,t) = C_0 \sin(\pi x/l)\exp(-t/\tau)$$

where $\tau(t) = l^2/\pi^2 D$.

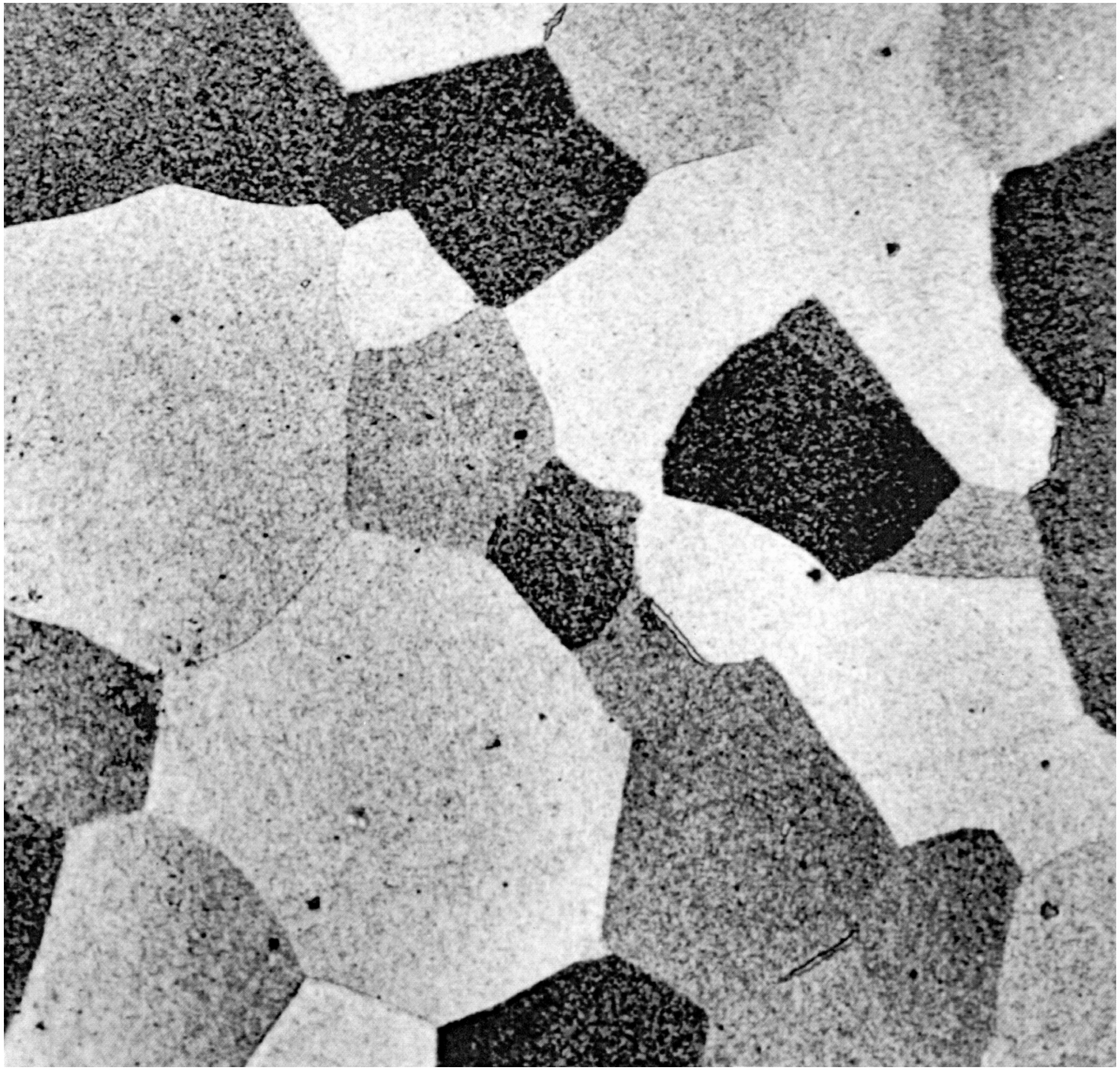


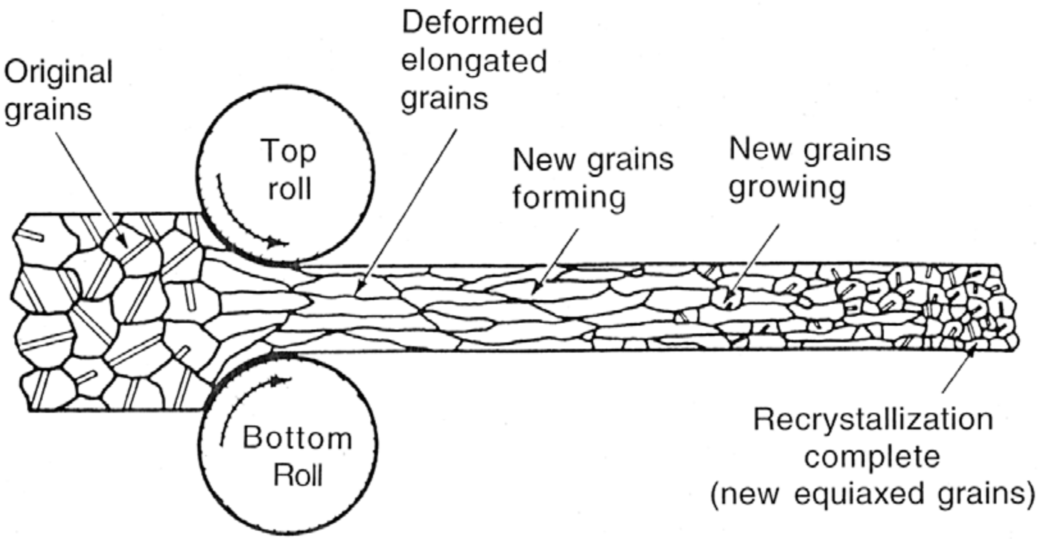
Homogenization at 450⁰C

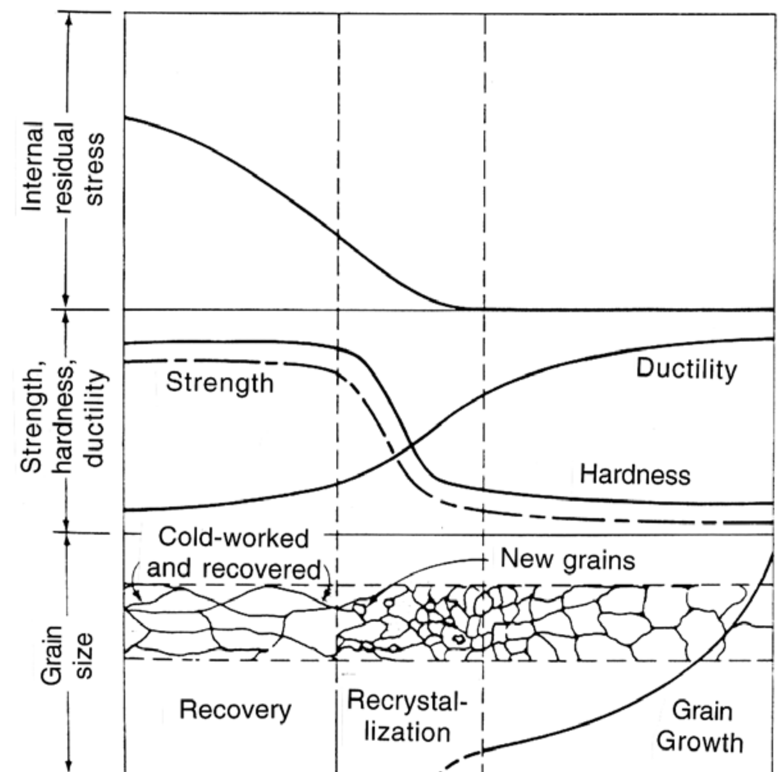


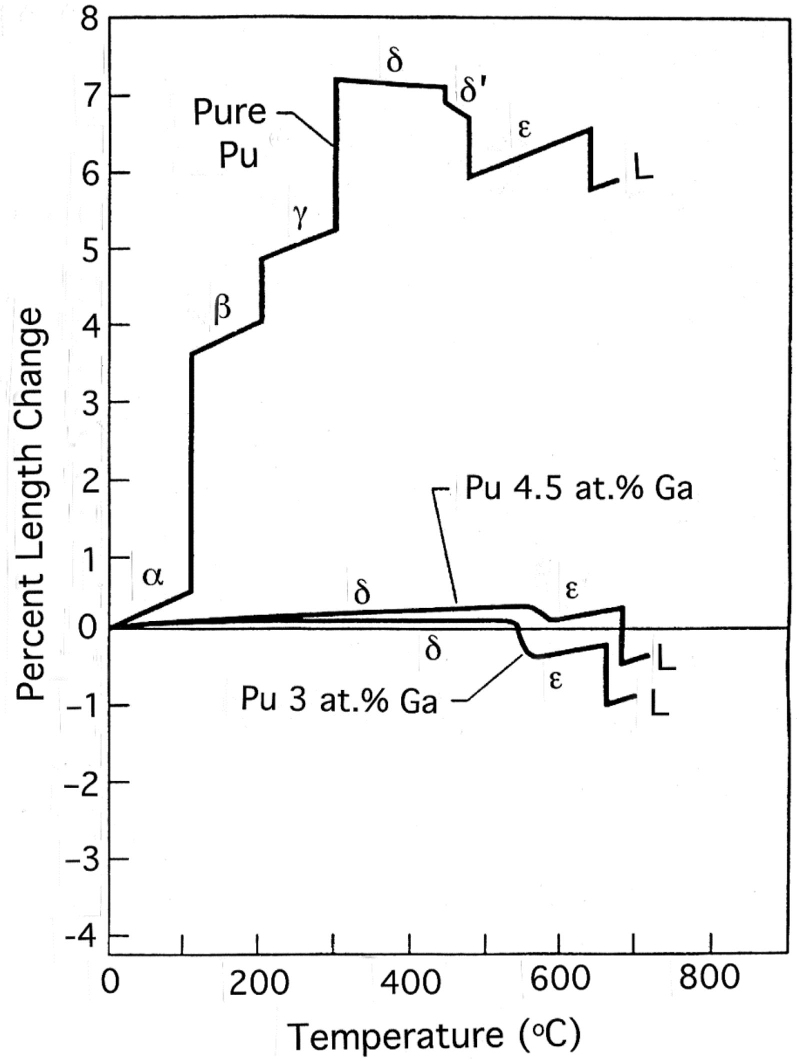


The Homogenized Pu-Ga Alloy is a Single Phase FCC Alloy

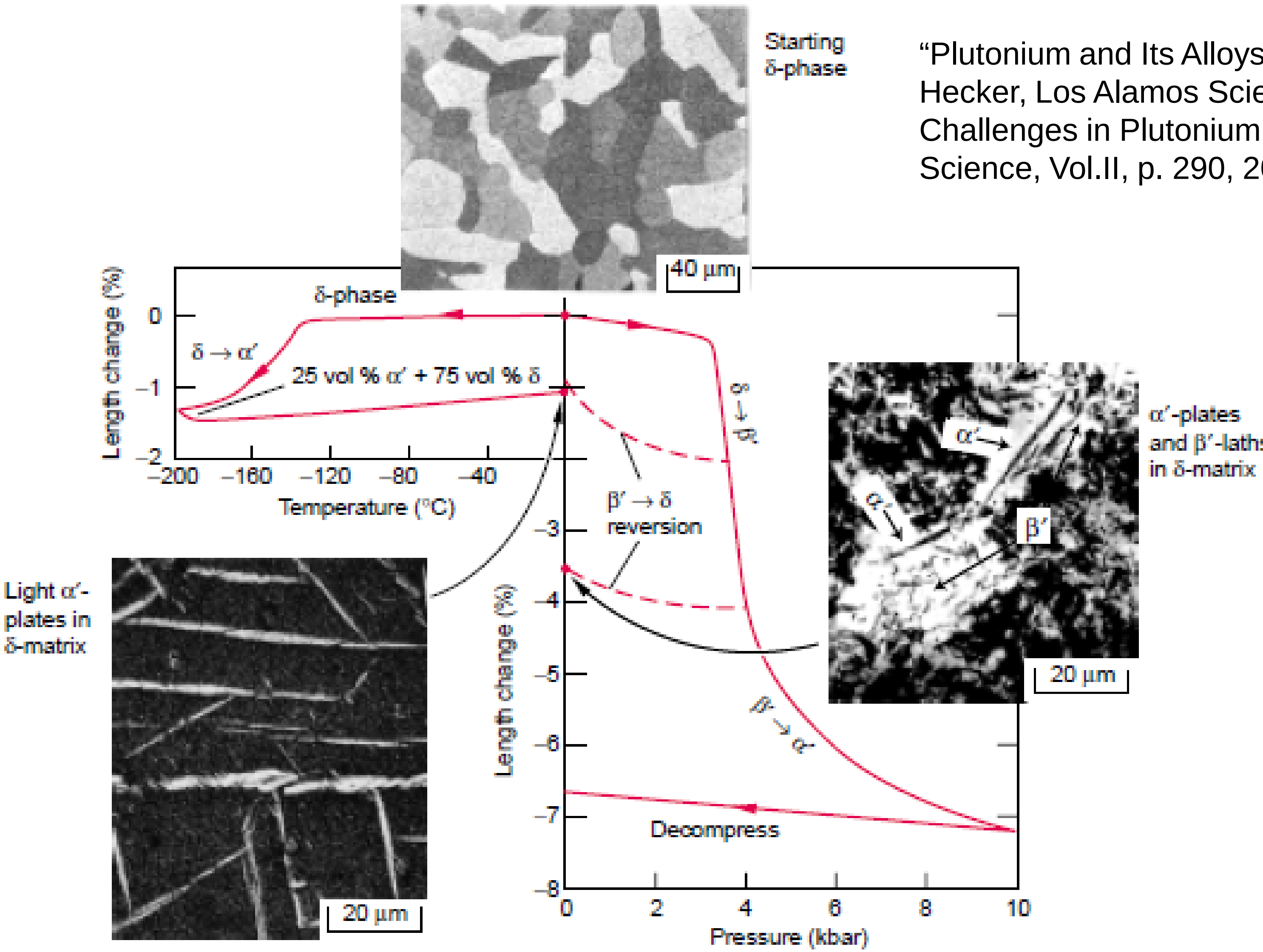



Original grains
Deformed elongated grains
New grains forming
New grains growing
Top roll
Bottom Roll
Recrystallization complete (new equiaxed grains)


Internal residual stress
Strength, hardness, ductility
Grain size
Strength
Ductility
Hardness
Cold-worked and recovered
New grains
Recovery
Recrystal-lization
Grain Growth



Pure Pu
α
β
γ
δ
δ'
ε
L
Pu 4.5 at.% Ga
δ
ε
L
Pu 3 at.% Ga
δ
ε
L
Percent Length Change
8
7
6
5
4
3
2
1
0
−1
−2
−3
-4
0
200
400
600
800
Temperature (°C)



"Plutonium and Its Alloys", S. Hecker, Los Alamos Science: Challenges in Plutonium Science, Vol.II, p. 290, 2000.

Conclusions:

- Due to its nuclear properties, Pu will remain a material of global interest well into the future.
- Processing, Structure, Properties and Performance remains a good framework for discussion of Pu materials science
- Self-irradiation and aging effects continue to be central in discussions of Pu metallurgy
- Pu in its elemental form is extremely unstable, but alloying helps to stabilize Pu; but, questions remain as to how and why this stabilization occurs.
- Which is true Pu-Ga binary phase diagram: US or Russian?
- Metallurgical issues such as solute coring, phase instability, crystallographic texture, etc. result in challenges to casting, processing , and properties modeling and experiments.
- For Ga alloyed FCC stabilized Pu, temperature and pressure remain as variables impacting phase stability.

Thank you for your interest!