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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

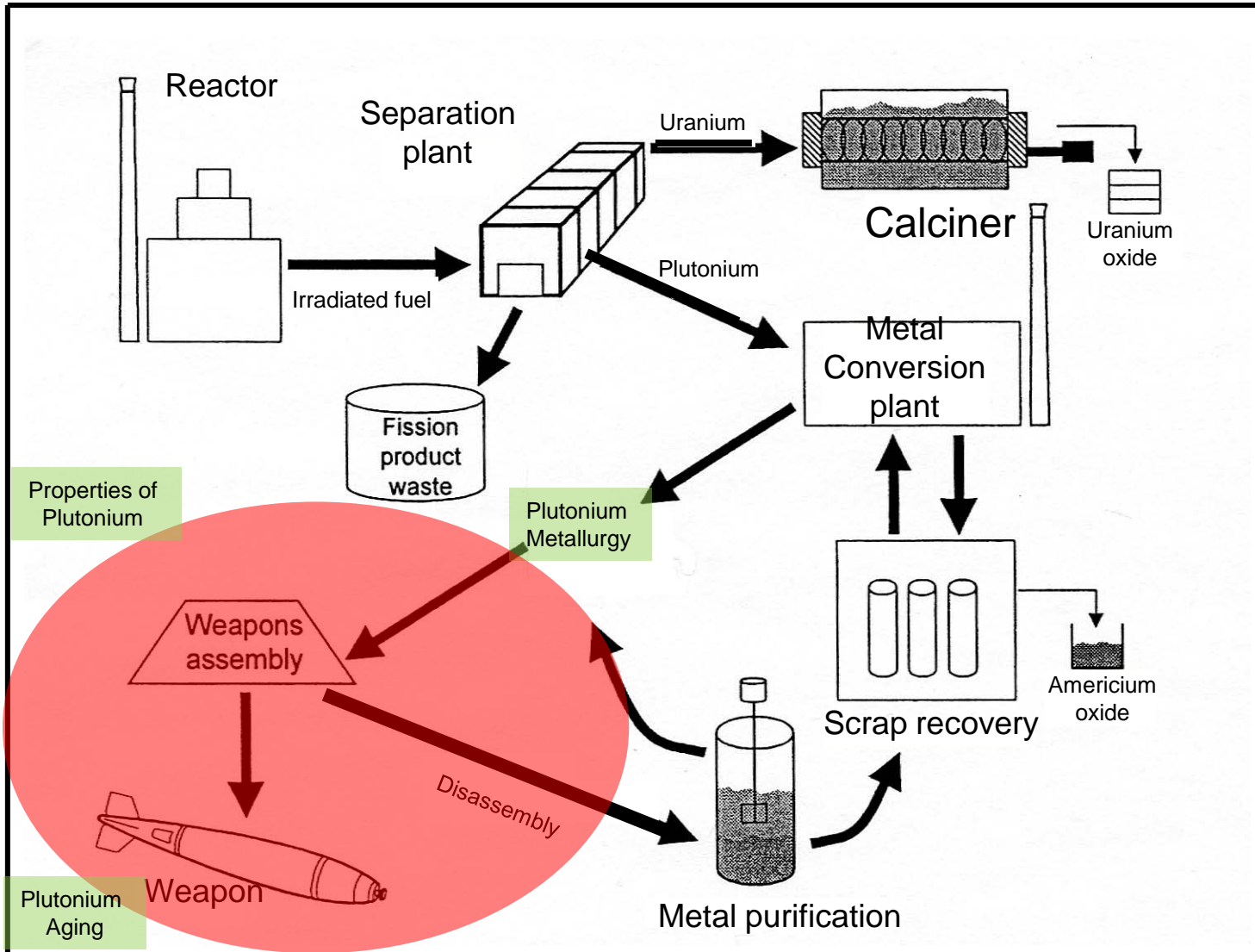


Plutonium Applications

All stem from special nuclear properties of Pu

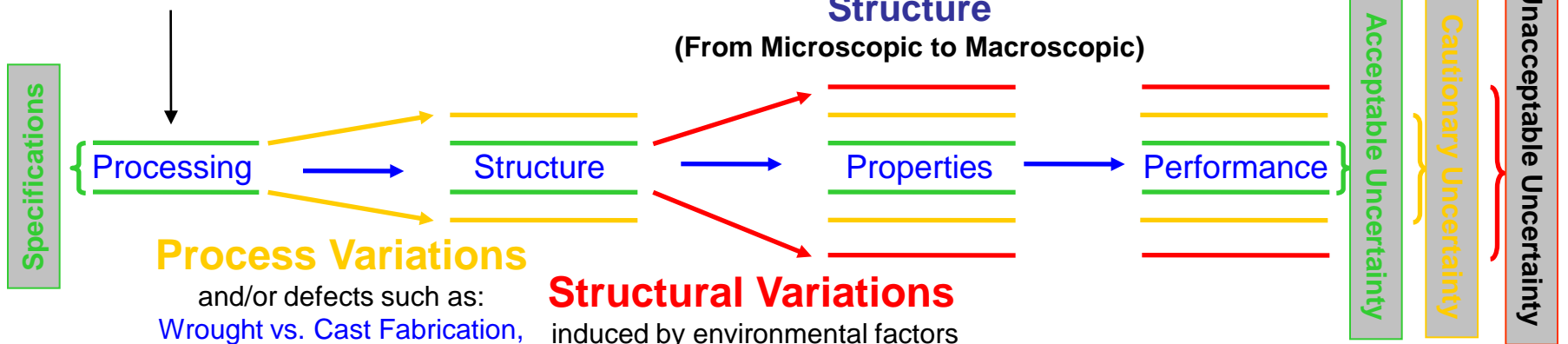
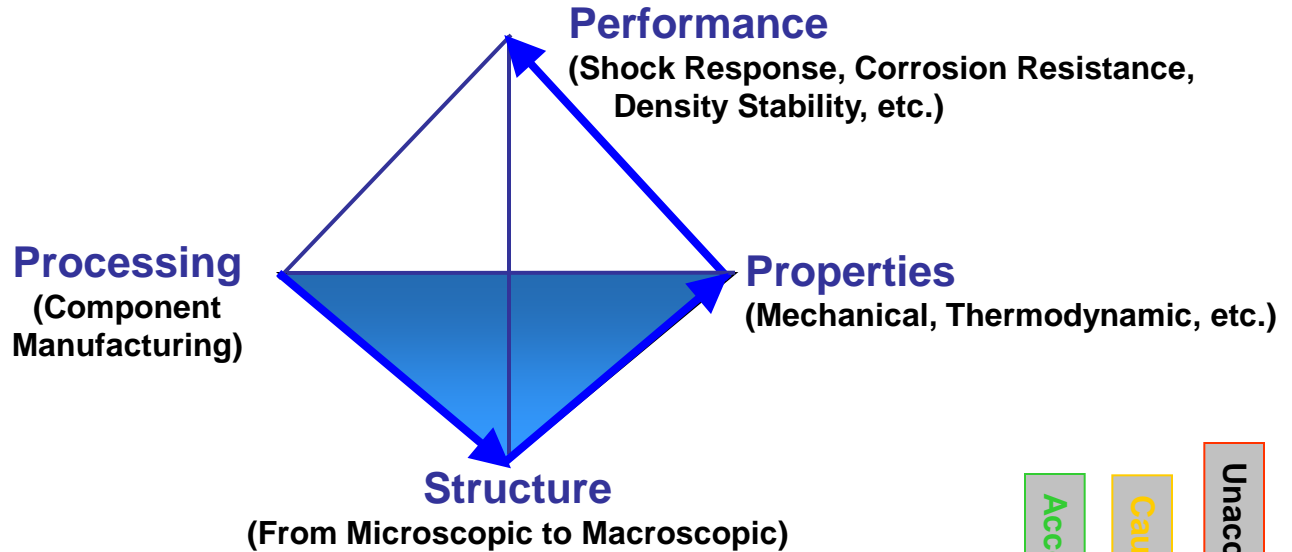
- | | |
|---|---|
| ^{239}Pu Metal : | Nuclear weapons
Early nuclear reactors |
| ^{239}Pu Oxide : | Nuclear reactors
Mixed oxide fuels
$^{238}\text{UO}_2$-20%$^{239}\text{PuO}_2$ |
| ^{238}Pu Oxide : | Radioisotope heat sources
Fuel for space power systems |

Plutonium Processing Cycle



Materials Science Tetrahedron Applied to Weapons Materials

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



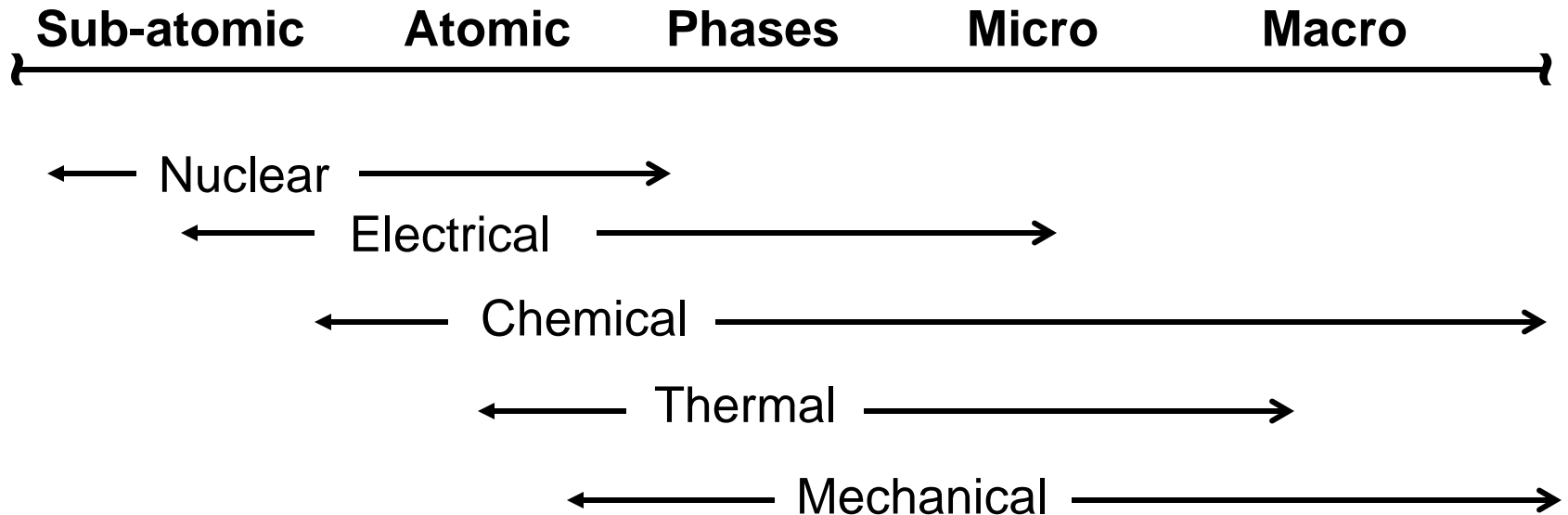
Process Variations
 and/or defects such as:
 Wrought vs. Cast Fabrication,
 Casting Asymmetries and/or
 Impurities and Inclusions
lead to structural variations.

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

STRUCTURE



PROPERTIES

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Liquid Nuclear Fuels Data

LA-2958
CHEMISTRY--GENERAL
(TID-4500, 19th Ed.)

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)

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. GLASS, T. A. SANDANAYAKE, and C. C. HERRICK

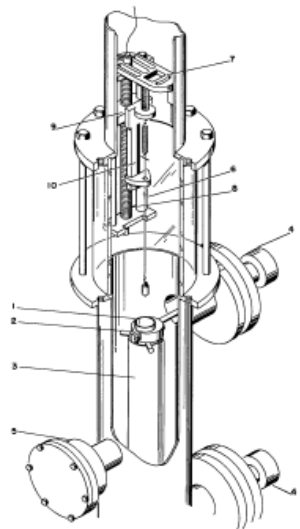


Fig. 1. Top of furnace and measuring apparatus.

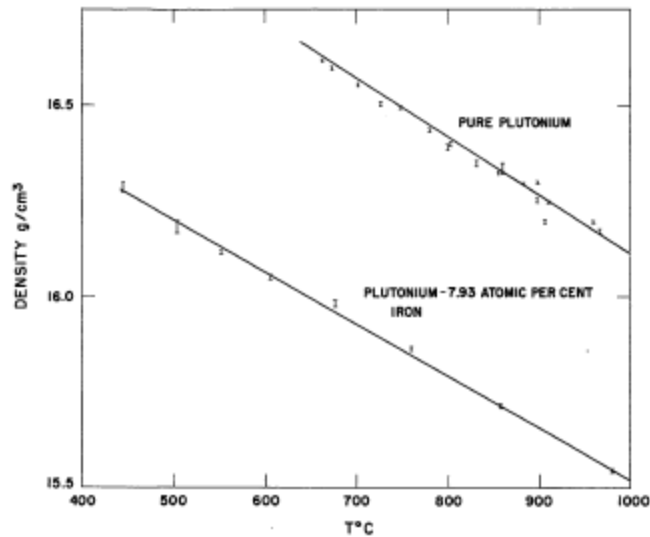


Fig. 2. Density vs temperature of plutonium-iron alloy.

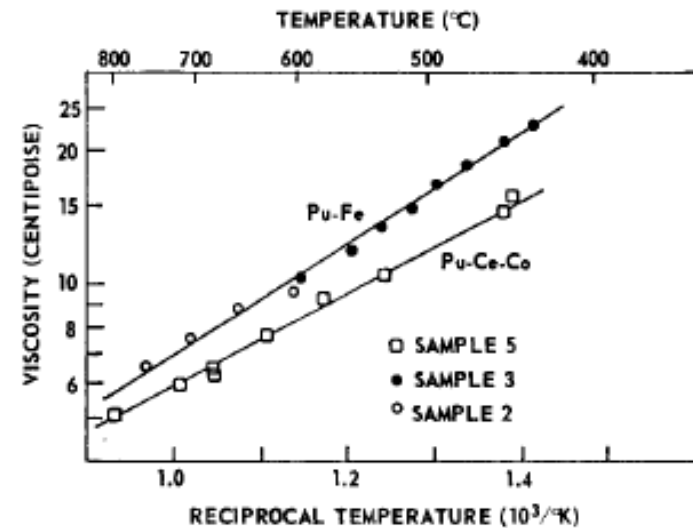


FIG. 6. Logarithm of viscosity as a function of reciprocal temperature for plutonium-iron and plutonium-cerium-cobalt alloys.

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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)

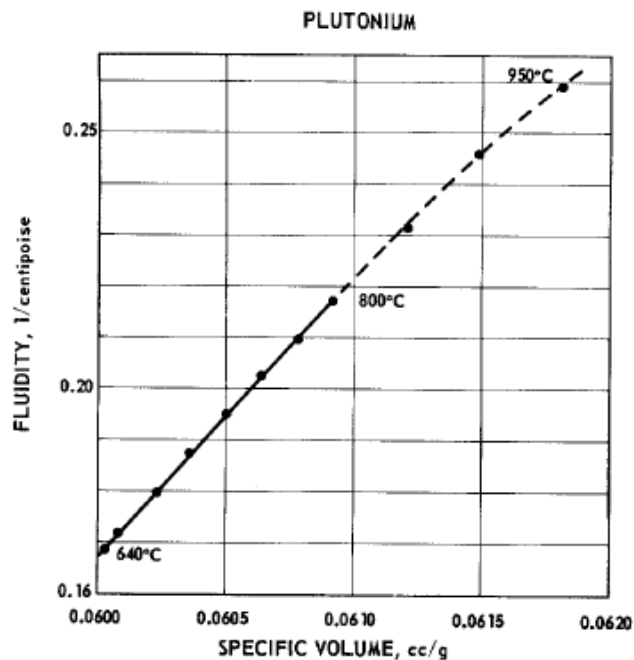


FIG. 2. Fluidity as a function of specific volume for liquid plutonium.

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

$$\bar{\Delta}V_f = (V_l - c)$$

Anomalous
Low-density
Solid

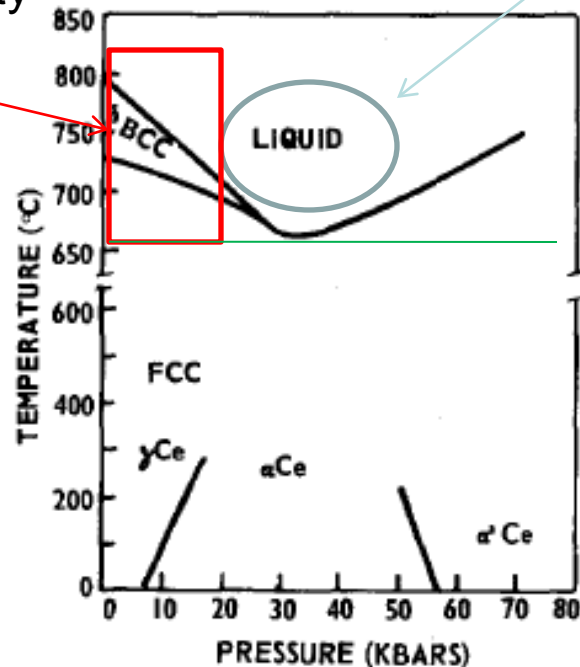


FIG. 6. Phase diagram of cerium (Ref. 16).

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

Plutonium Applications: MOX Fuels

THE PLUTONIUM-OXYGEN AND URANIUM-PLUTONIUM-OXYGEN SYSTEMS:

A THERMOCHEMICAL ASSESSMENT

REPORT OF A PANEL ON THERMODYNAMICS
OF PLUTONIUM OXIDES
HELD IN VIENNA, 24-28 OCTOBER 1966

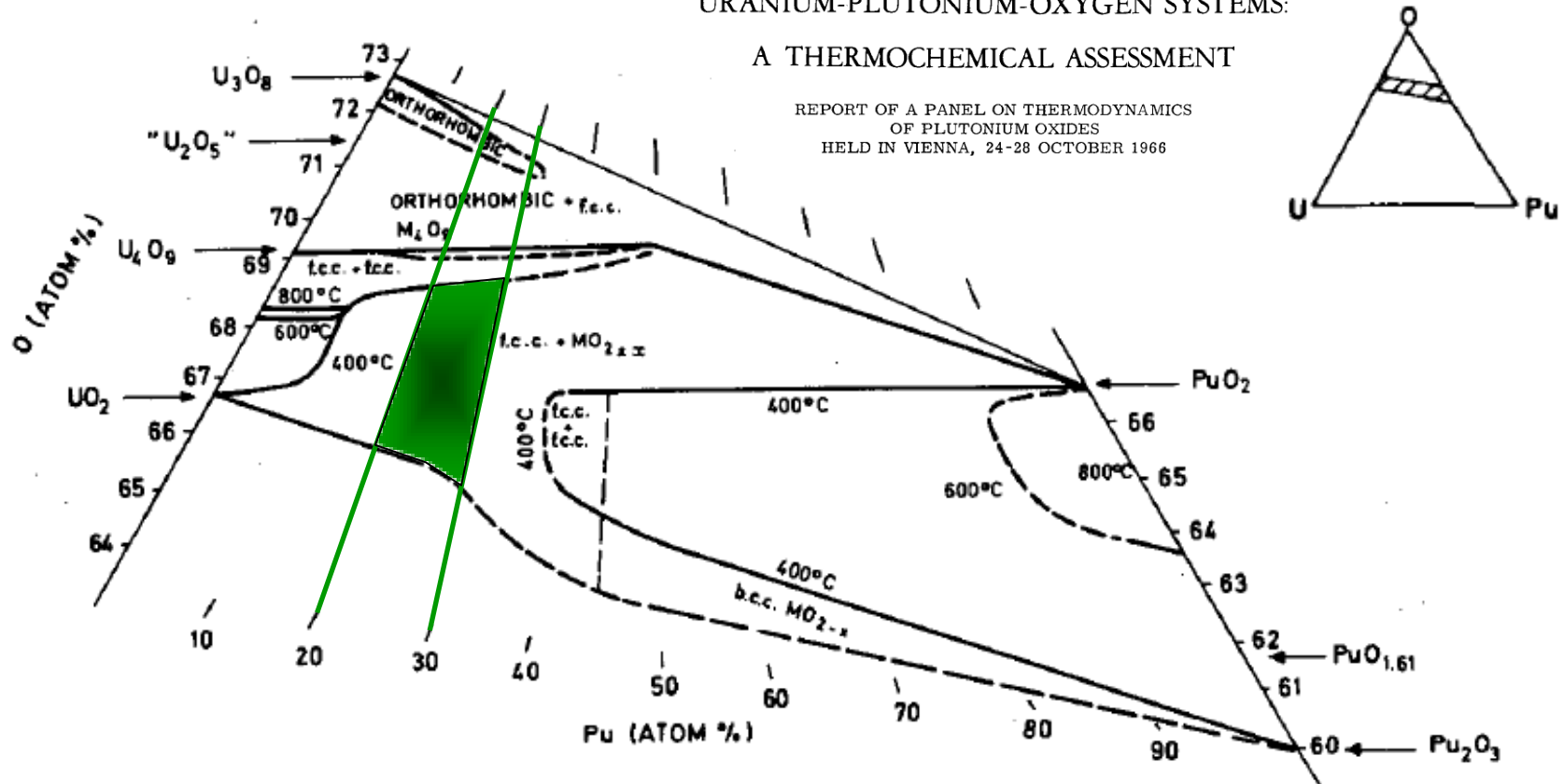
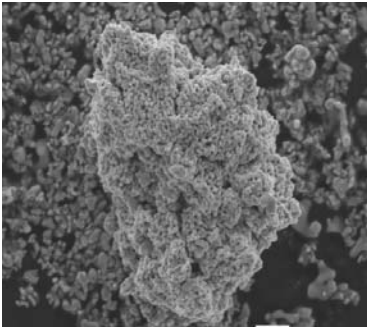


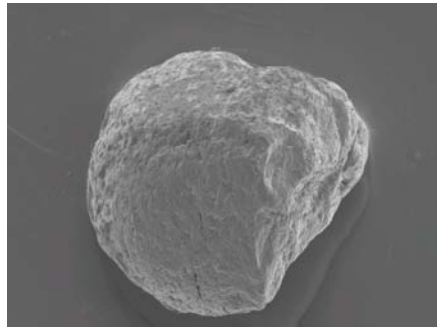
FIG. 13. U-Pu-O ternary section at 400, 600 and 800°C.

MAMOX: Precursor Oxide Particle Morphology and Fuels Microstructure

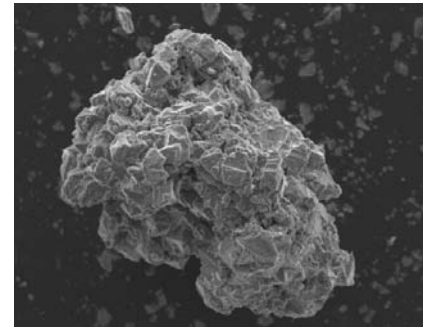
DUO_2 11,000x



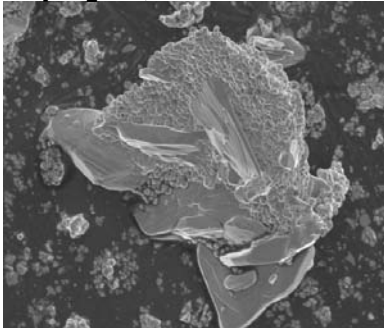
HEUO_2 1,400x



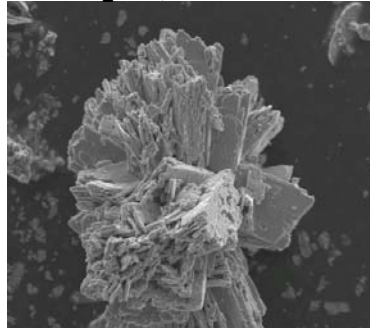
PuO_2 3,500x



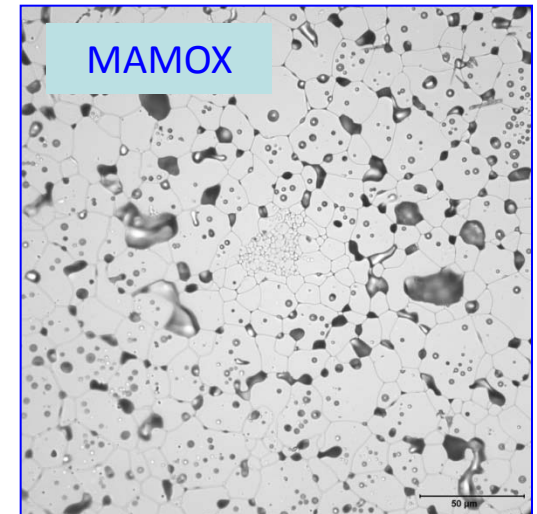
NpO_2 2,300x



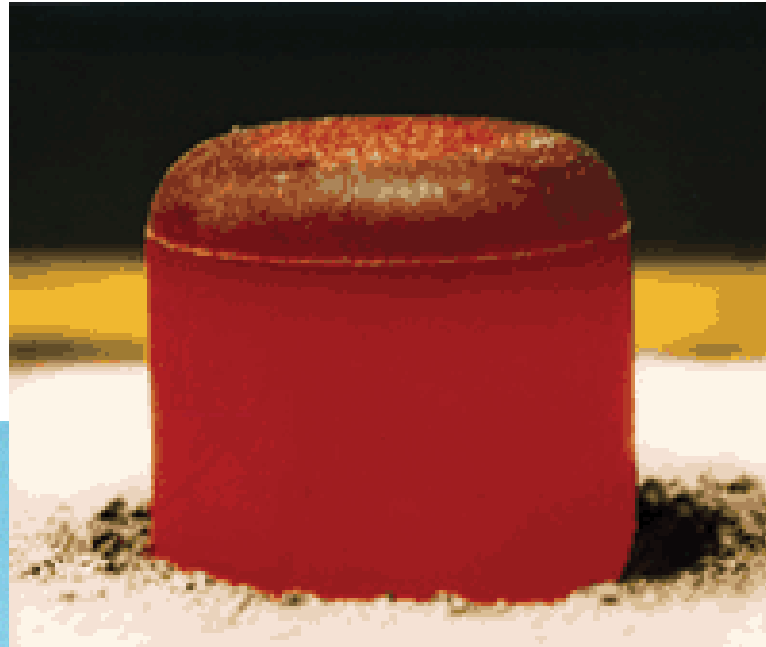
AmO_2 4,000x



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

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Pu Self-Irradiation and Induced Aging Effects



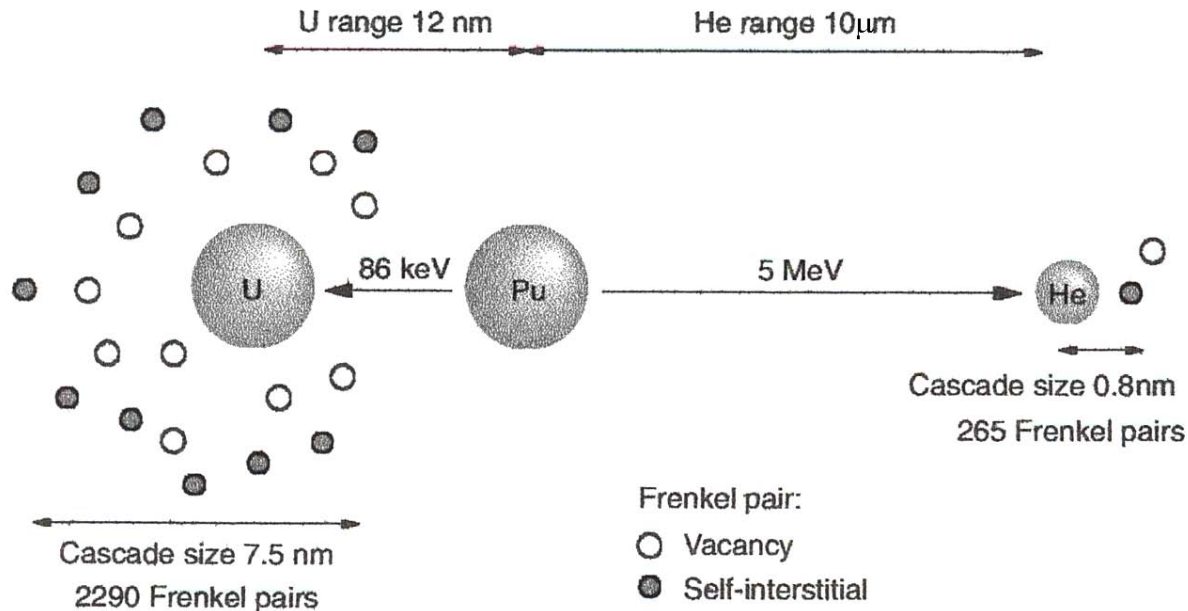
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Plutonium Isotopes, Half-Lives and Typical Materials

Isotope Mass #	T_{1/2} Half-life	Thermal neutron fission	Weapons Grade Plutonium (%)	Accelerated Aging (%)	Reactor Grade Plutonium (%)	Heat Source (%)
Pu²³⁸	87.7 yrs	Probably	<0.05	7.5	1.5	90.0
Pu²³⁹	24,100 yrs	Yes	86.1	93.6	58.1	9.1
Pu²⁴⁰	6,560 yrs	No	6	6	24.1	0.6
Pu²⁴¹	14.4 yrs	Yes	0.4	0.4	11.4	0.03
Pu²⁴²	3.8 x 10⁵ yrs	No	<0.05	<0.05	4.9	<0.01
Pu²⁴⁴	8.0 x 10⁷ yrs	No	-	-	-	-

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

Radioactive Decay of Plutonium



Uranium: Energy Deposition: Significant (**85keV into 72,000 Unit Cells $\approx 1.2\text{meV}/\text{\AA}^3$**)
Residual Defect Structures: vacancies and interstitials
Inclusion Phases?: U complexes, Solute-Solvent Complexes (δ -phase alloys)

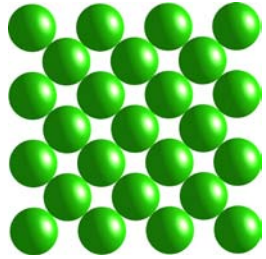
Alpha Particle: Energy Deposition: Minimal (**5Mev into 40×10^{12} Unit Cells $\approx 1.3\text{neV}/\text{\AA}^3$**);
Residual Defect Structures: not likely
Inclusion Phases: He Bubbles

Perspective: Atoms to Bulk

			<u>Type of Defect</u>
Relative Dimensions	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"

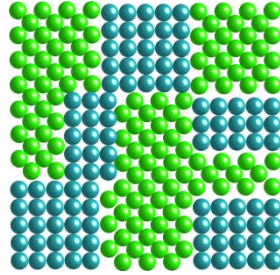
Plutonium Aging: Length Scales and Properties

Atomic scale ~ 10 Å



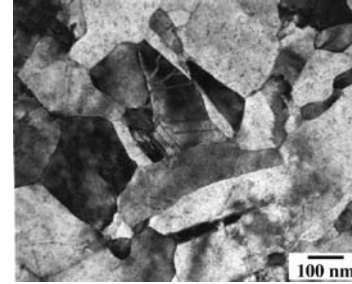
atomic structure

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

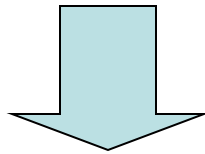
Controlling effects of heterogeneities, **process coupling** (chem, phys, mech)

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

Effects of Alpha Particle Decay Branch

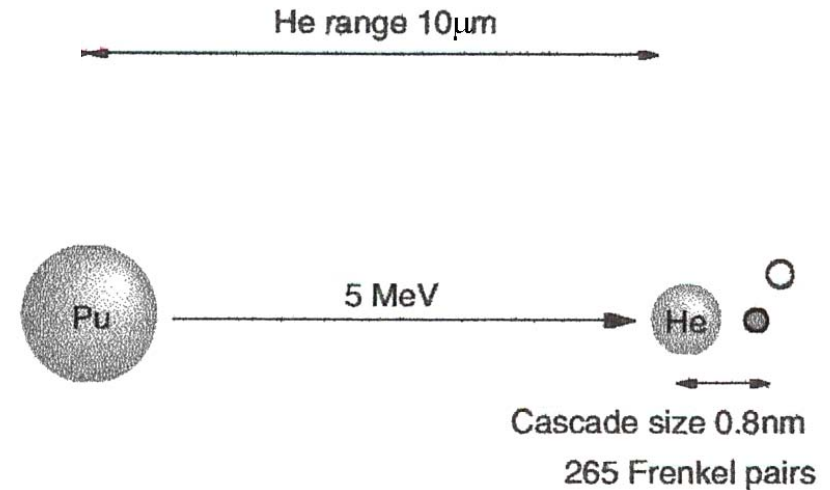
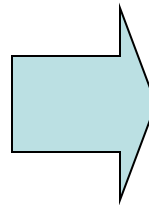
Nanoscale:

- 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

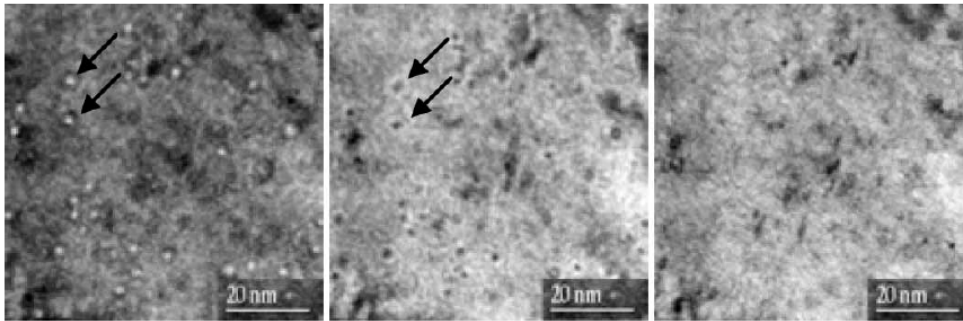


Figure 1. TEM images of 42-year-old Pu alloy. (a) The $-1.4\mu\text{m}$ under-focus bright-field TEM micrograph shows a high number density of very small helium bubbles as a dark fringe surrounding a light dot. (b) The $+1.4\mu\text{m}$ over-focus image reveals the bubbles as light fringes surrounding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

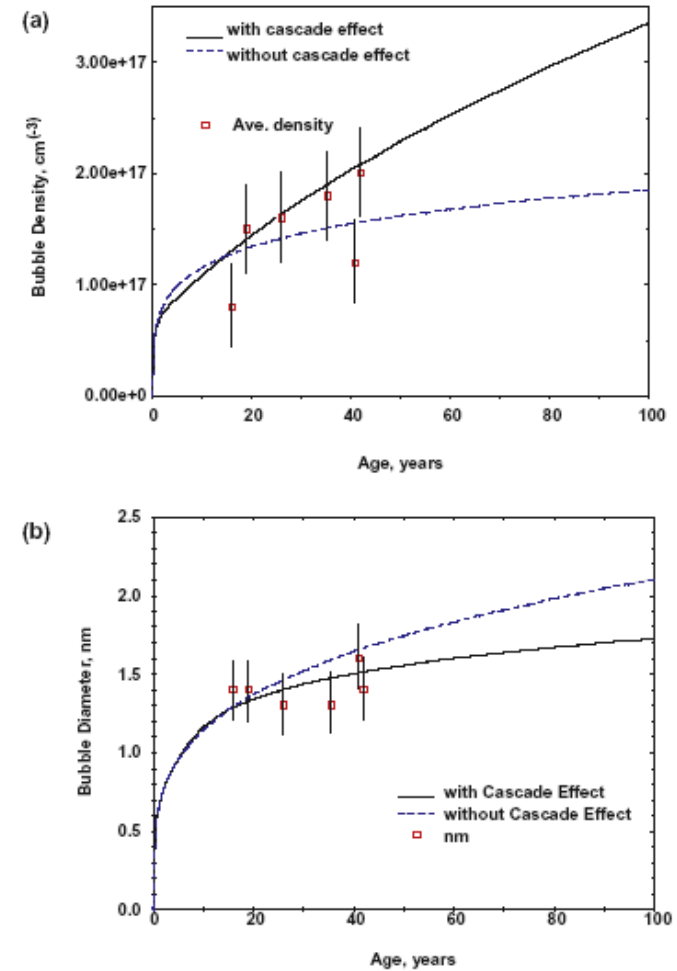
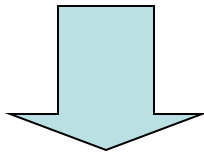


Figure 6. (a) Predicted helium bubble density and (b) average bubble diameter as a function of the plutonium age or the helium content (411 ppm He is generated in 10 years).

Effects of Uranium Decay Branch

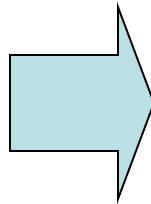
Nanoscale:

- 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.



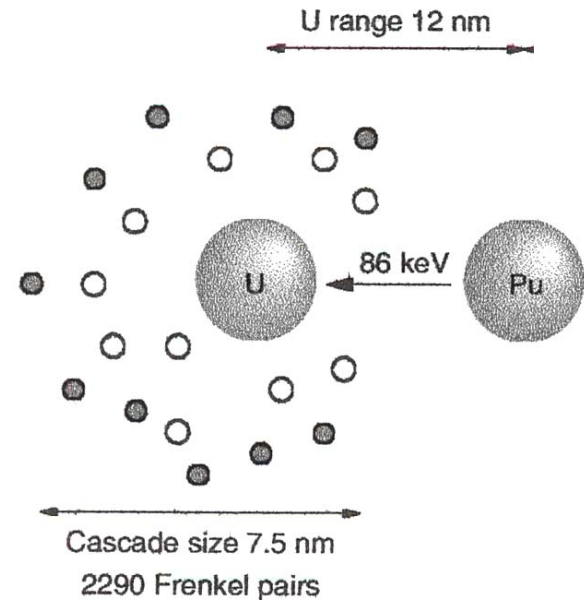
Microscale:

- Defects pin dislocations; and
- Defect generated strain field impedes $\delta \rightarrow \alpha'$ transformation.

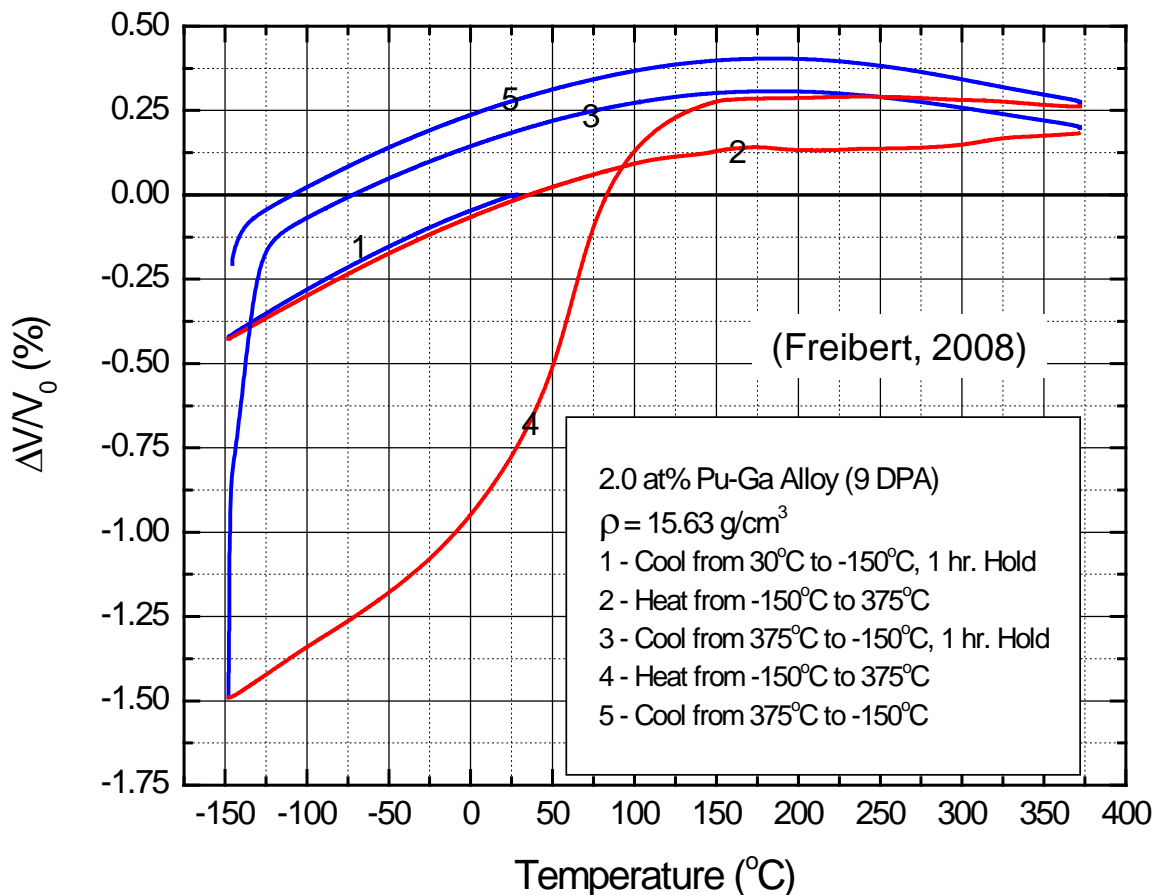


Macroscale:

- Volume swelling from damage to point of saturation;
- Aging related mechanism increases yield 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 $\delta \rightarrow \alpha'$.

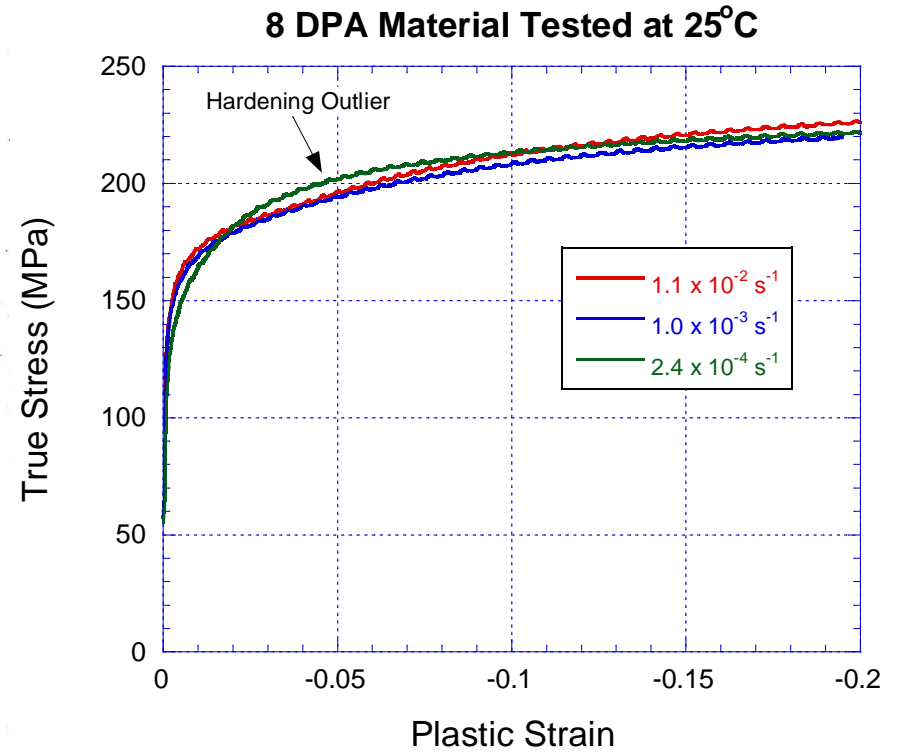
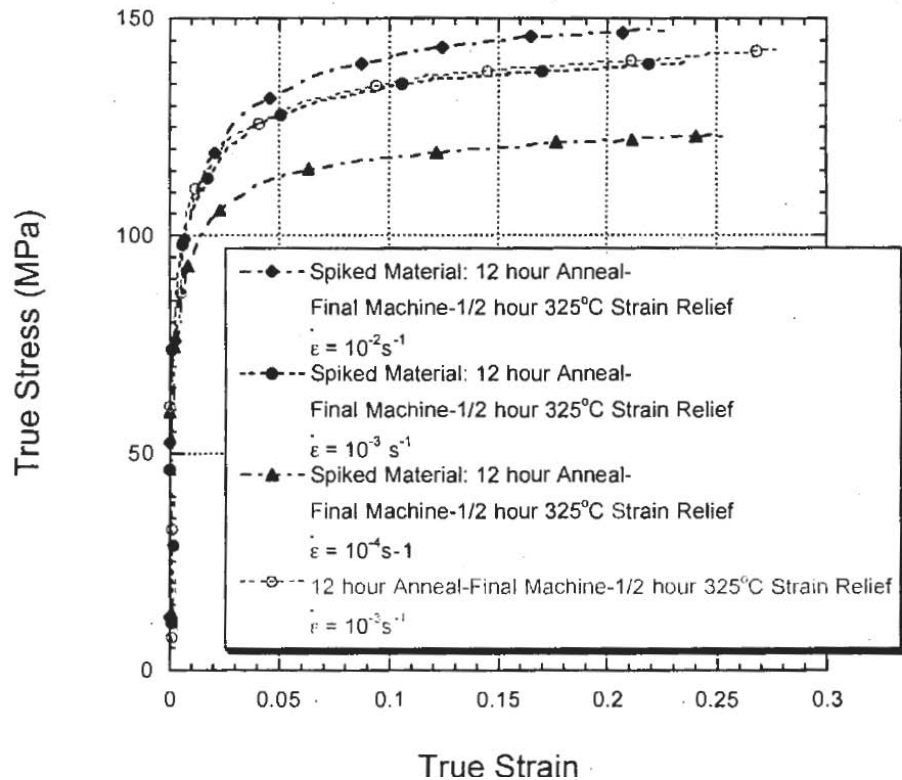
After damage anneals ($T > 150^\circ\text{C}$), $\delta \rightarrow \alpha'$ occurs in agreement with 0.6 w/o Ga alloy (Hecker, 2001): Transformation Onset: -130°C .

Full reversion ($\alpha' \rightarrow \delta$) occurs from -150 to 150°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.

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Unalloyed Plutonium Structural, Thermodynamic and Mechanical Properties

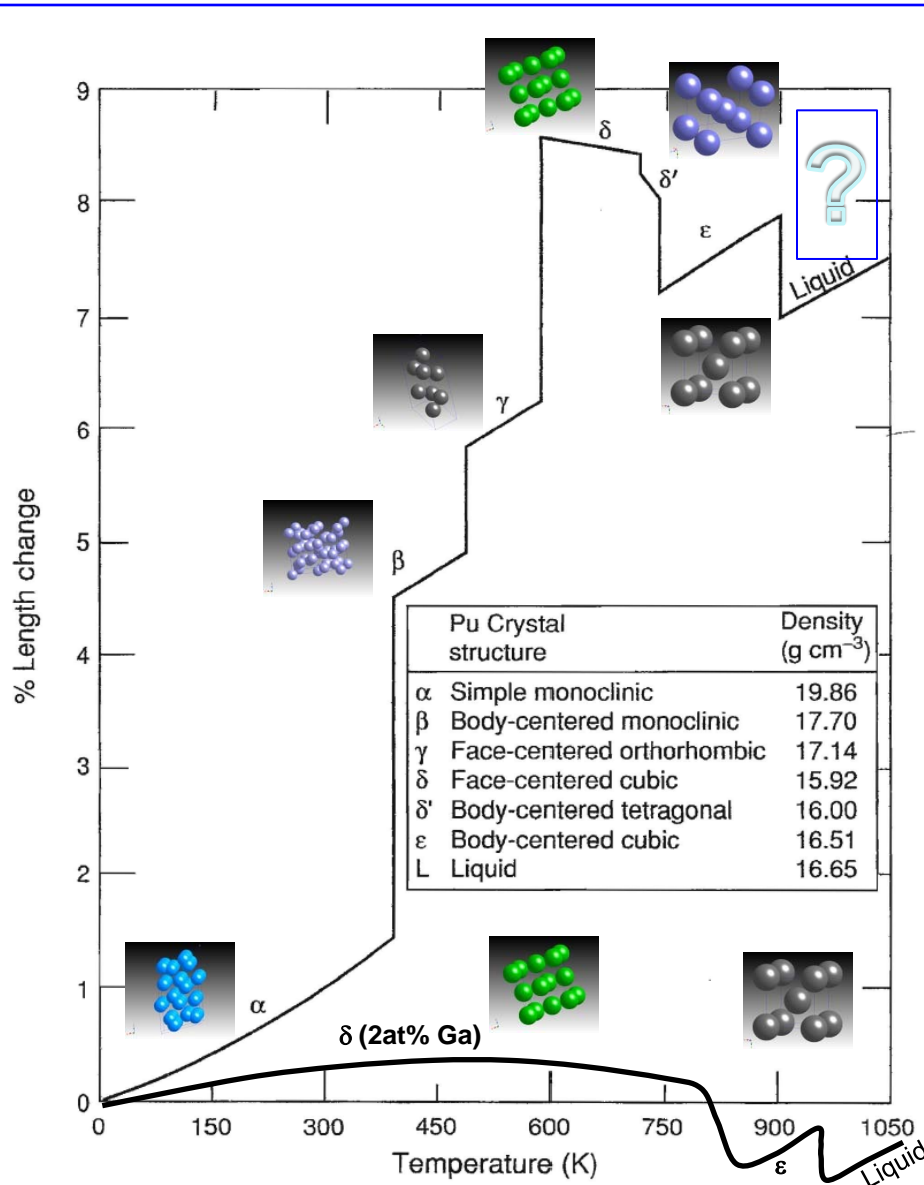


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Crystal Structure Data for Plutonium

Phase	Stability Range °C	Space Lattice and Space Group	Unit Cell Dimensions, Å	Atoms per unit Cell	X-ray Density, gm/cm ³
α	Below ~115	Simple monoclinic <i>P2₁/m</i>	@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>I2/m</i>	@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 <i>Fddd</i>	@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, <i>Fm3m</i>	@320 °C: a= 4.6371 ±0.004	4	15.92
δ'	452-480	Body-centered tetragonal <i>I4/mmm</i>	@465 °C: a= 3.34 ±0.01 c= 4.44 ±0.04	2	16.00
ϵ	480-640	Body-centered cubic, <i>Im3m</i>	@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
 - Pu₆Fe 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:

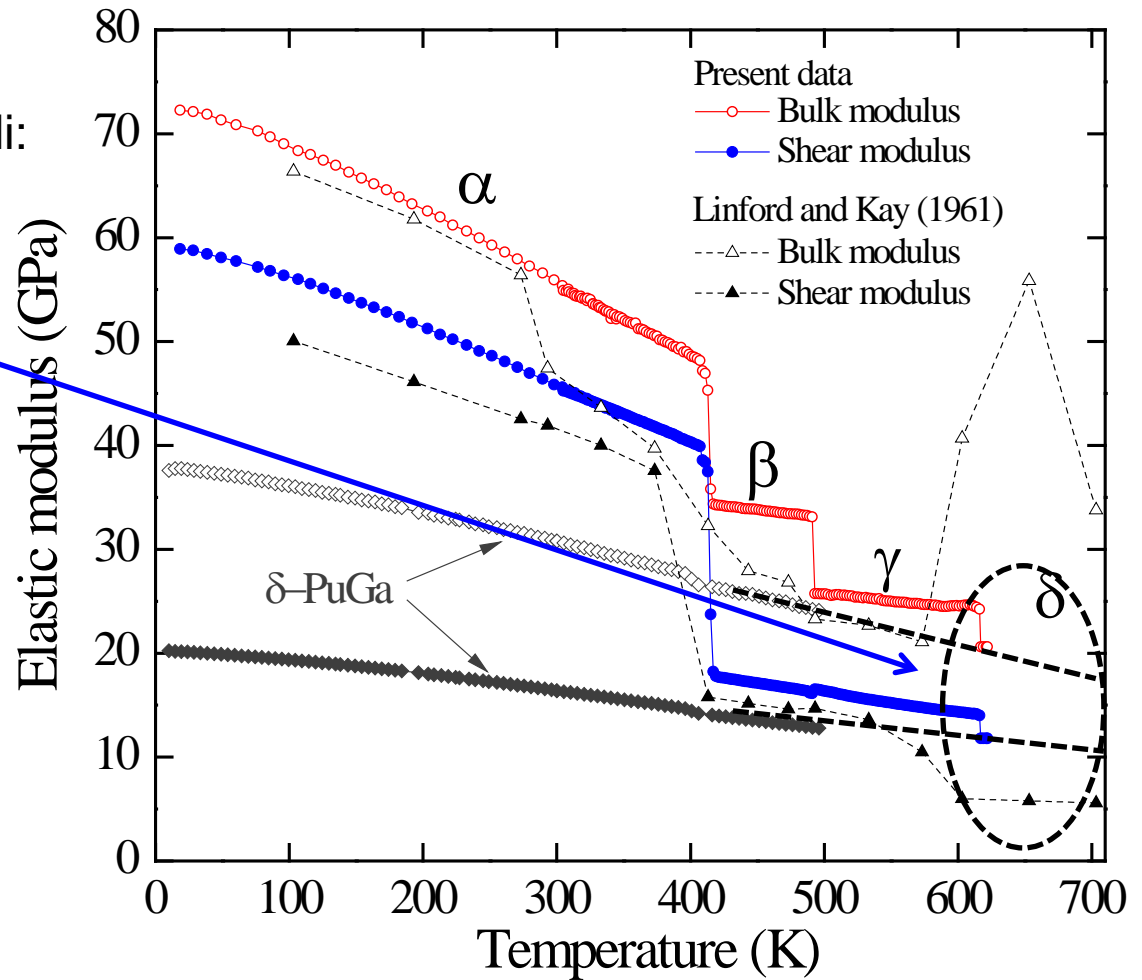
$$B_{\delta\text{-Pu}} = 20.6 \text{ GPa}$$

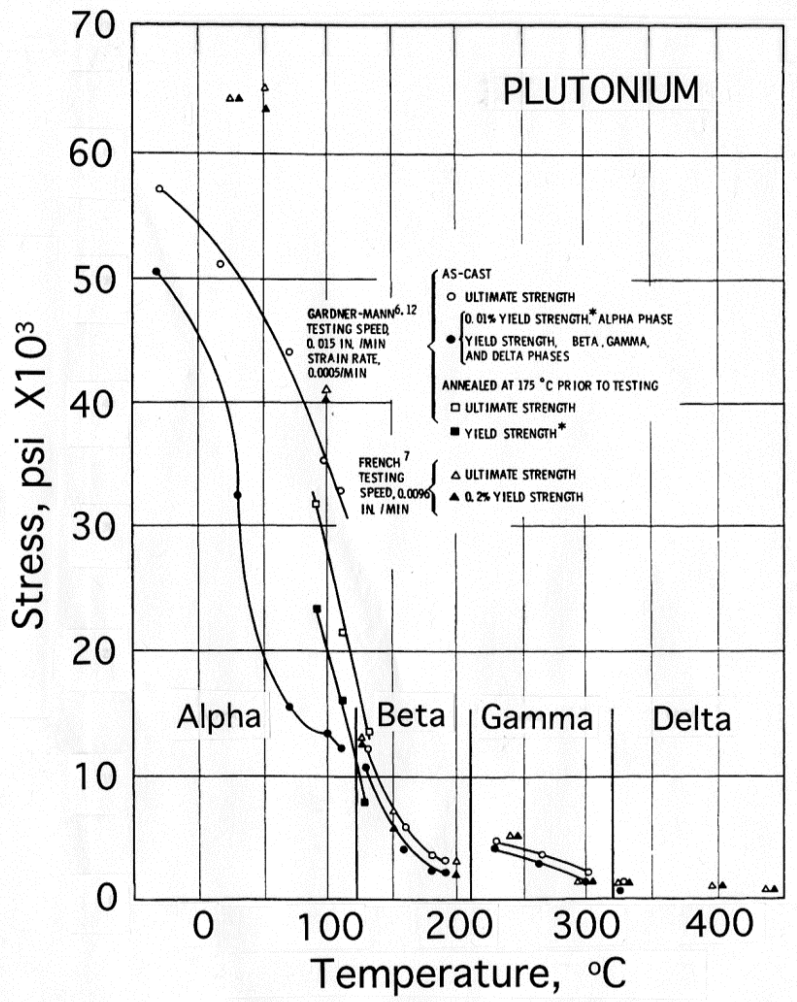
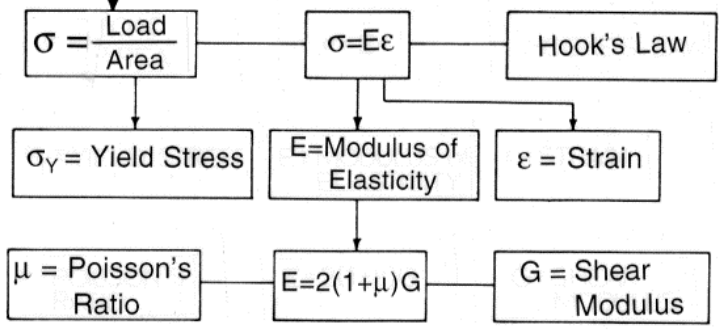
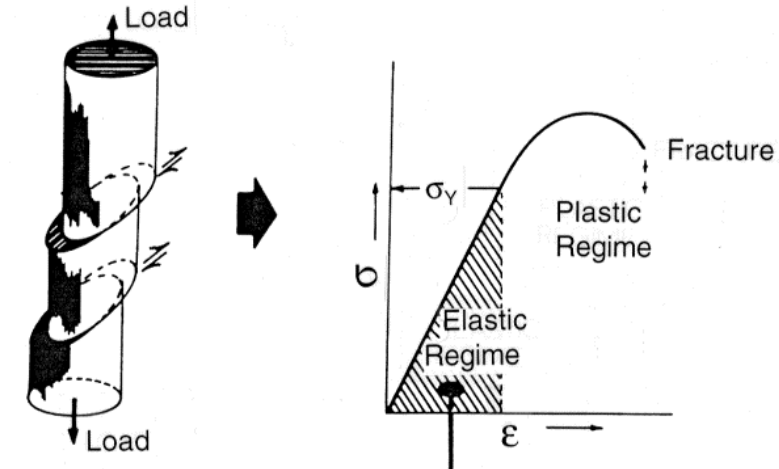
$$G_{\delta\text{-Pu}} = 11.8 \text{ GPa}$$

$$B_{\delta\text{-PuGa}}^{Ext.} = 22 \text{ GPa}$$

$$G_{\delta\text{-PuGa}}^{Ext.} = 12 \text{ GPa}$$

- $\alpha \rightarrow \beta$, $\beta \rightarrow \gamma$, and $\gamma \rightarrow \delta$ Pu transformation are continuous.
- β -Pu and γ -Pu exhibit the same shear modulus with a 30% variation in bulk modulus.





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Plutonium Alloys and Metallurgy



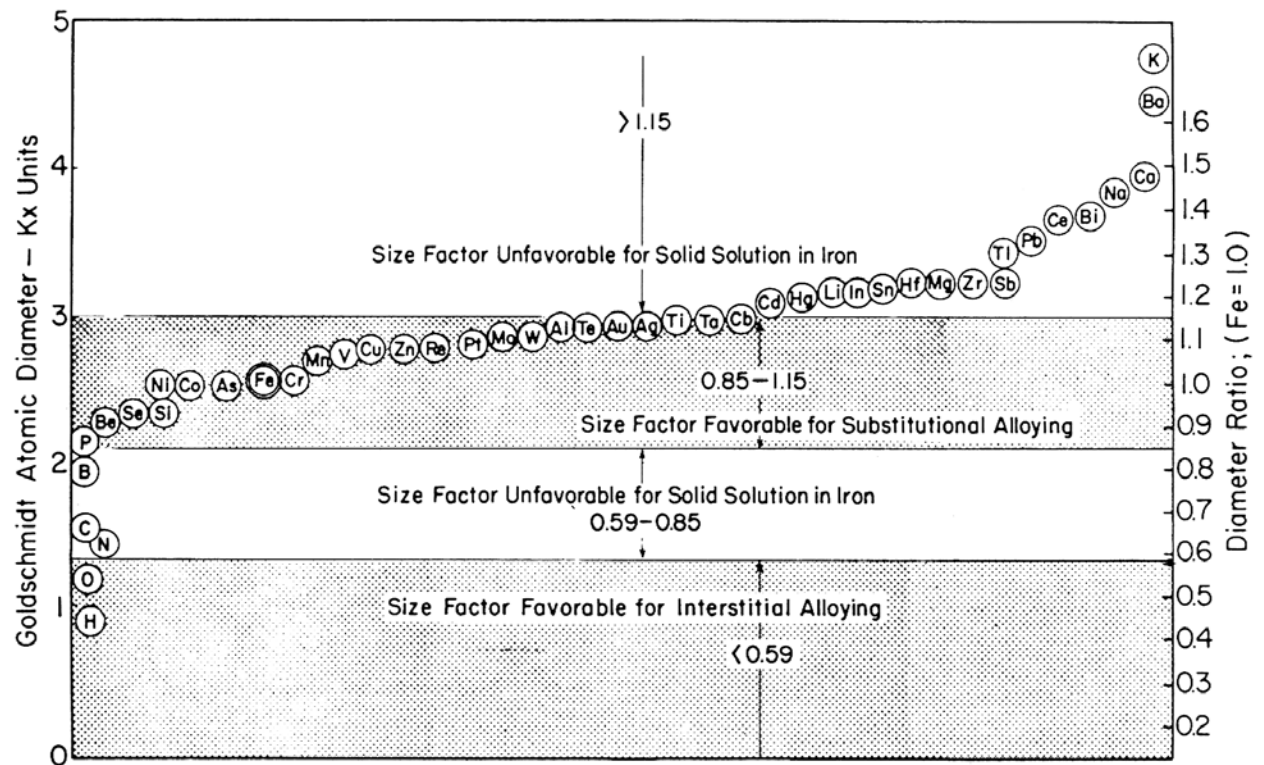
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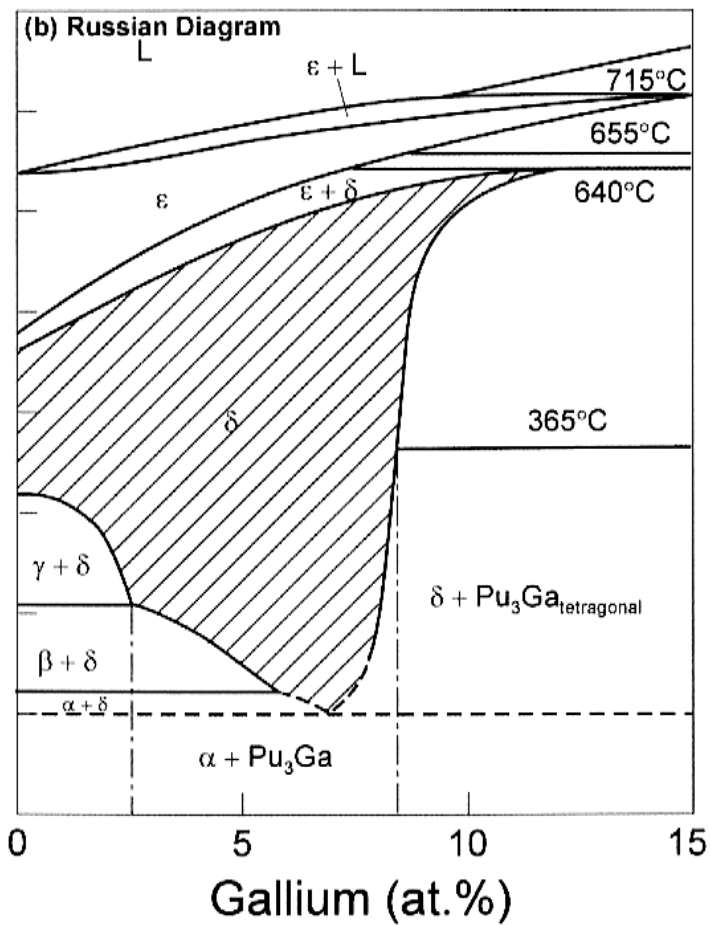
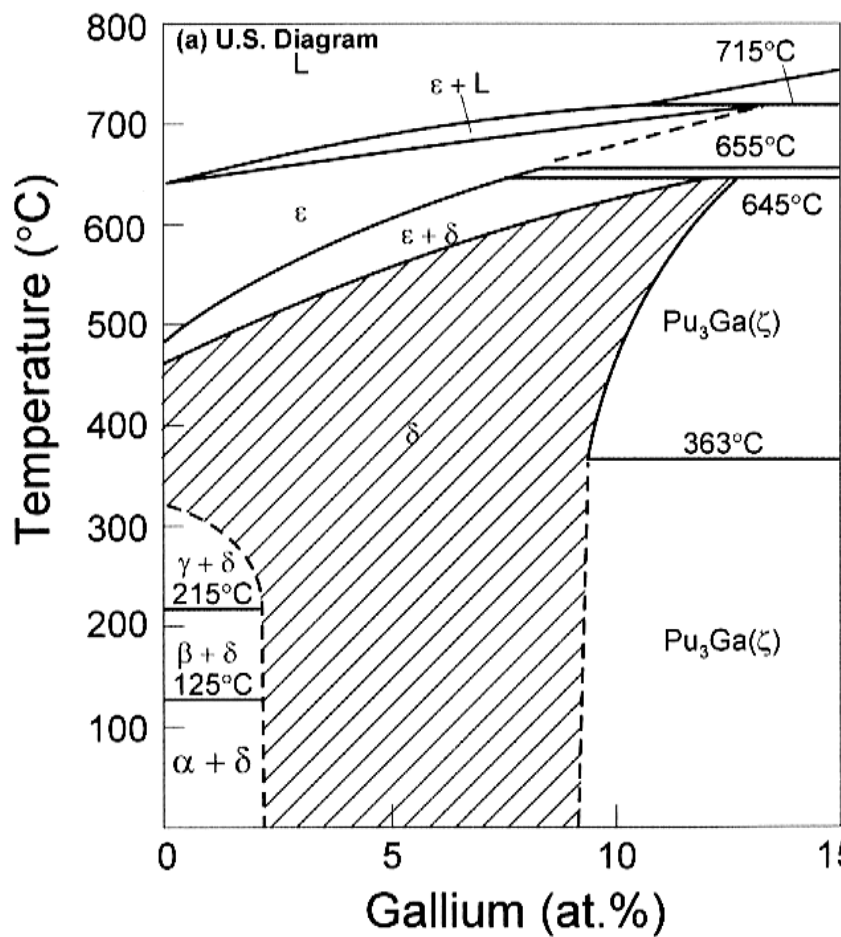
Elements that Alloy with Plutonium

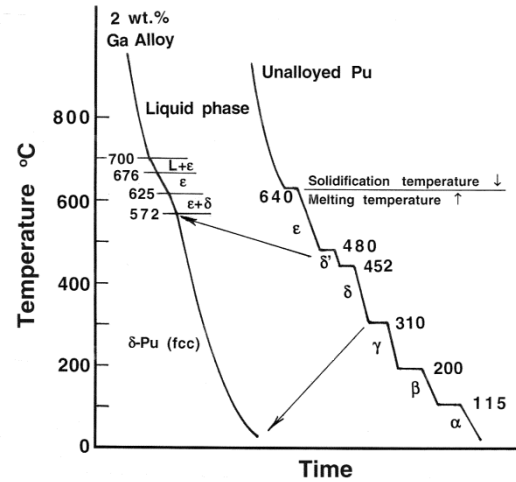
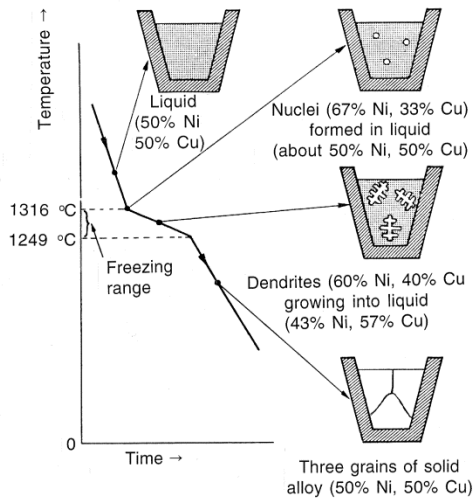
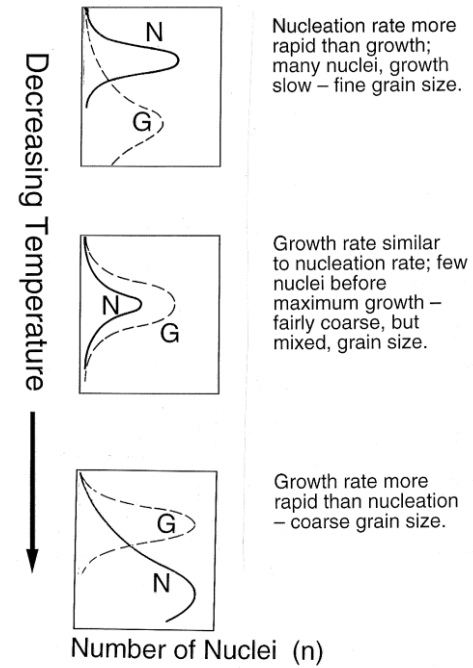
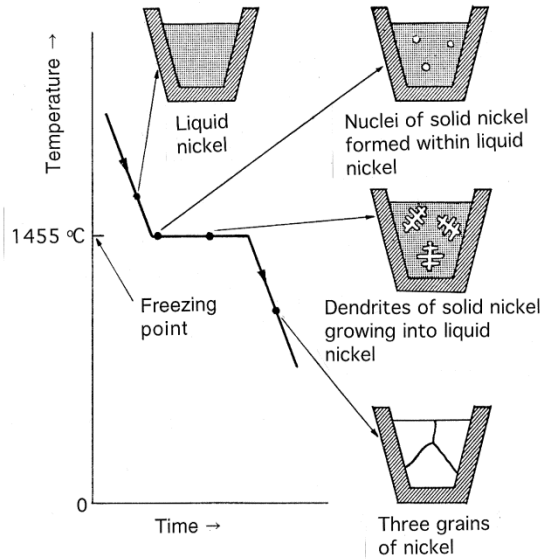
Phase		To R.T.	Not to R.T. (>1 wt. %)
α		Np, Ru, Zr	
β			Np, U, Zr
γ			Np, Th, U, Zr
δ		Al, Am, Ce, Ga, Sc	In, Np, Nd, Pm, Ru, Si, Sm, Th, Ti, U, Zn, Zr
δ'			Am, Np
ϵ			Ag, Al, Am, Ce, Cu, Dy, Er, Ga, Gd, Ho, In, Lu, Nd, Ni, Np, Os, Pd, Pm, Pr, Pt, Rh, Ru, Sc, Si, Sm, Th, Ti, Tm, U, Zn, Zr

Hume-Rothery Rules for Complete Solid Solubility and Alloying

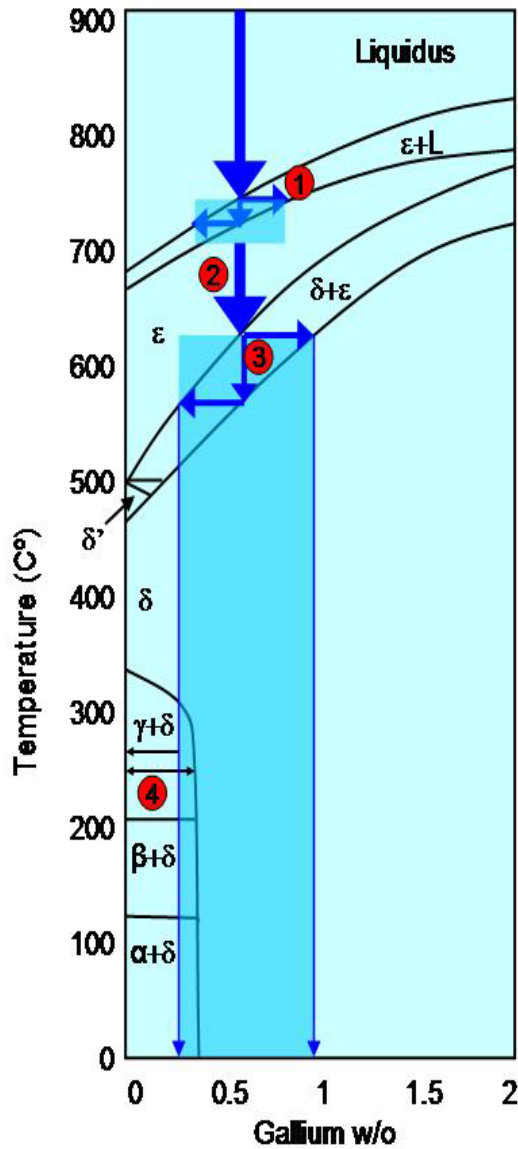
1. Must have the same crystal structure.
2. Less than $\pm 15\%$ difference in atomic radii.
3. Same valence.
4. Similar electronegativity.



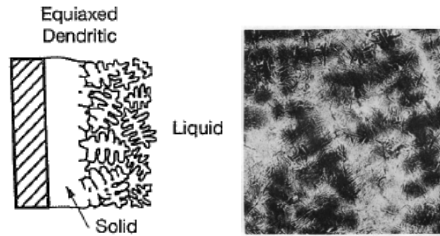




Casting Pu-Ga Alloys



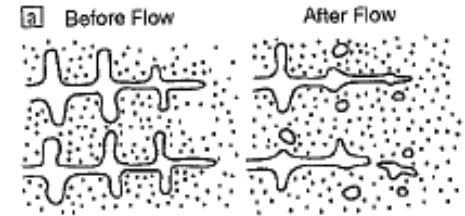
1



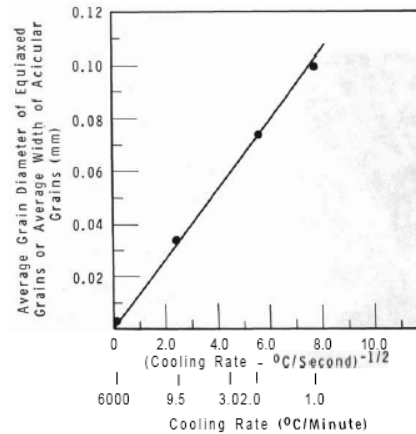
Solidification within $\epsilon+L$ phase field involves equiaxed dendrite formation initiated at the mold walls. Microsegregation of Ga or “coring” occurs.

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

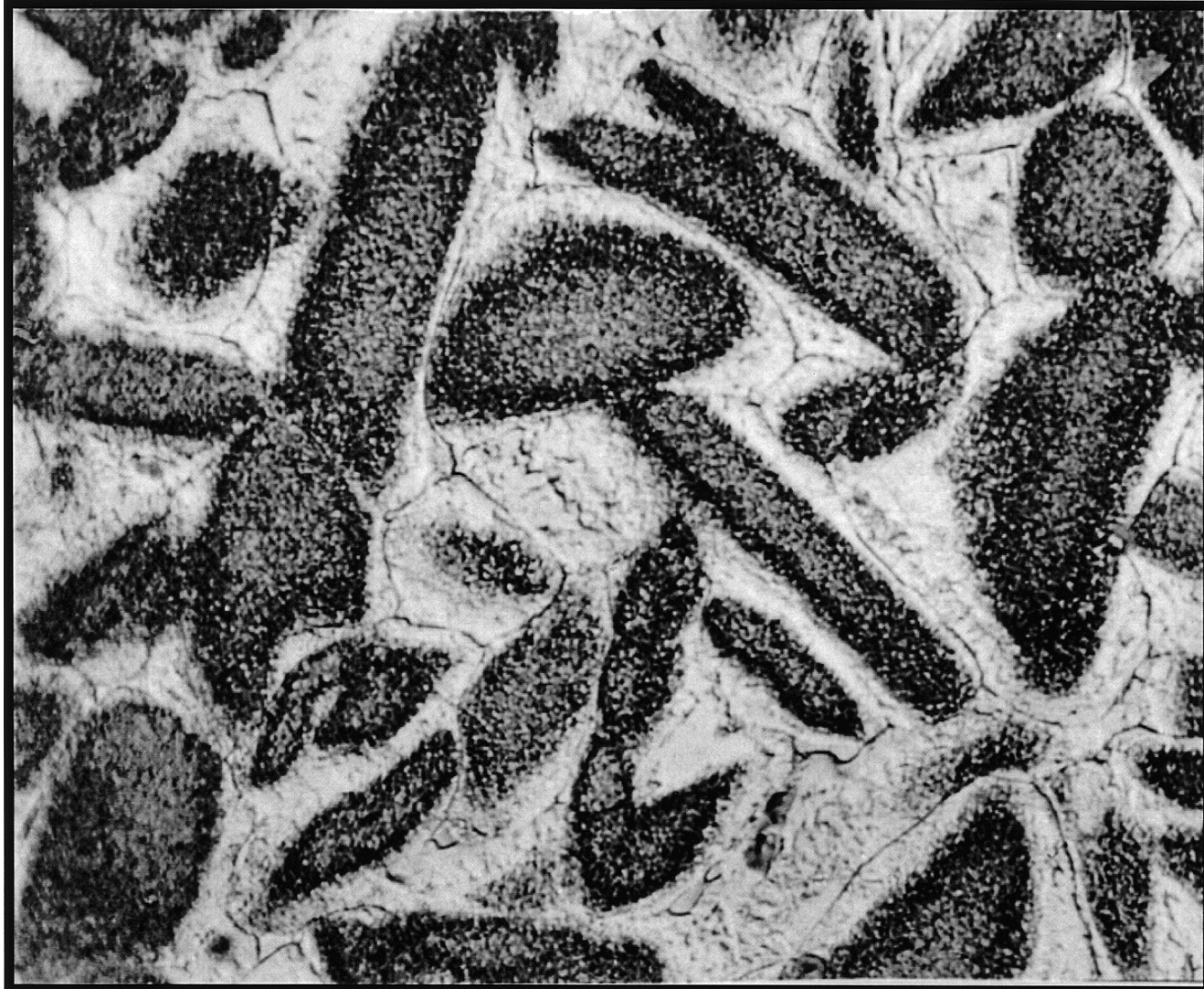


Microsegregation of Ga or “coring” occurs once again. Cooling rate through $\delta+\epsilon$ phase field determines final cored grains.

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

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 = ?

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

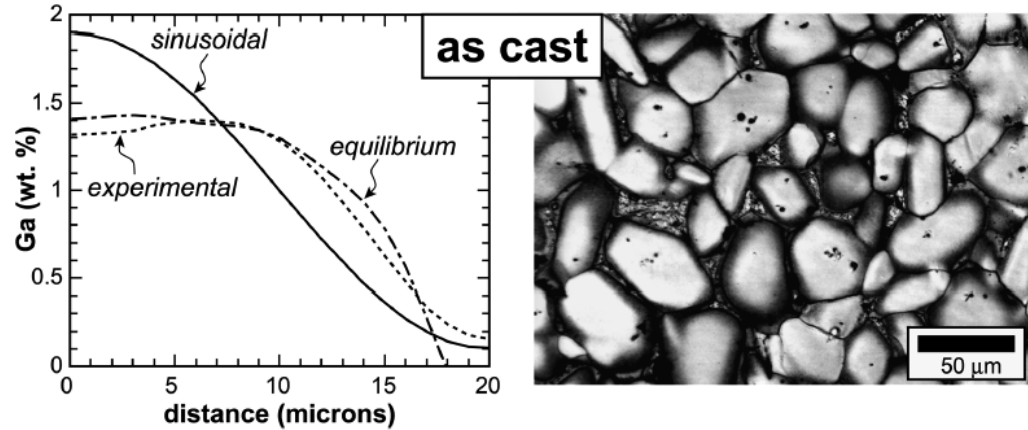
where $\tau(t) = l^2/\pi^2 D$.

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

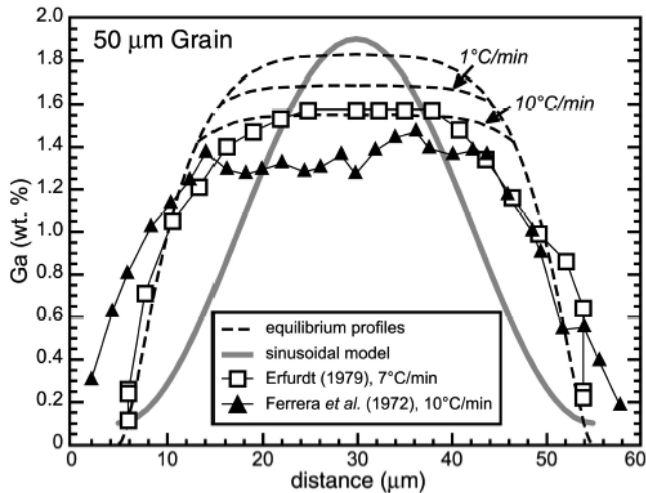
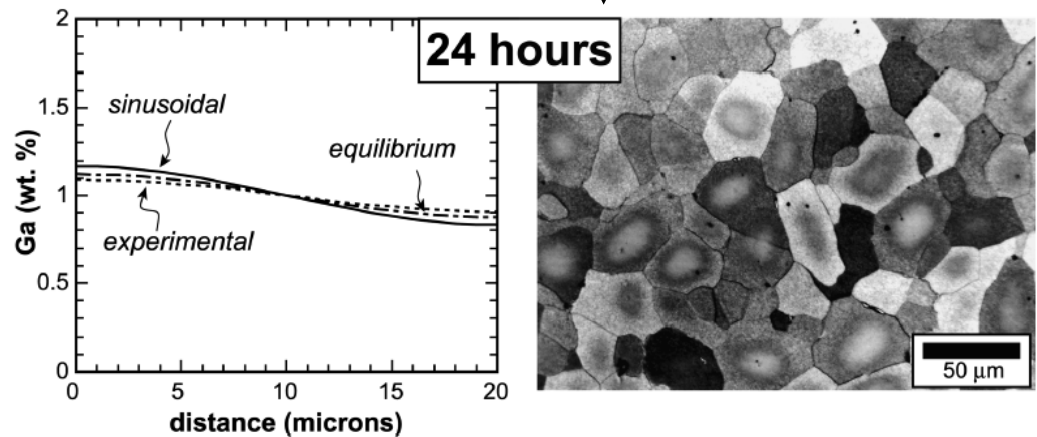
JEREMY N. MITCHELL, FRANK E. GIBBS, THOMAS G. ZOCCO, and RAMIRO A. PEREYRA

METALLURGICAL AND MATERIALS TRANSACTIONS A

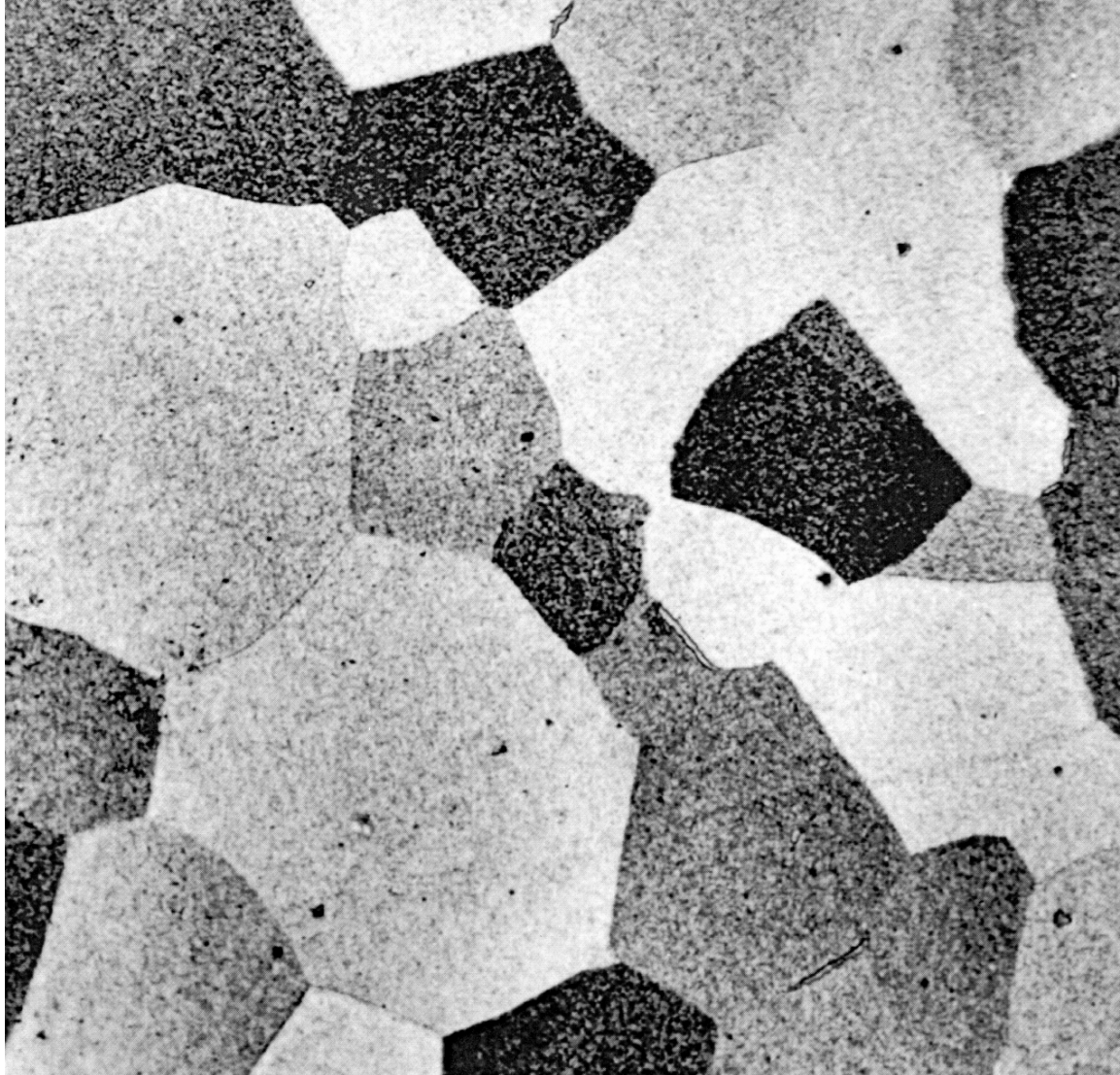
VOLUME 32A, MARCH 2001—649

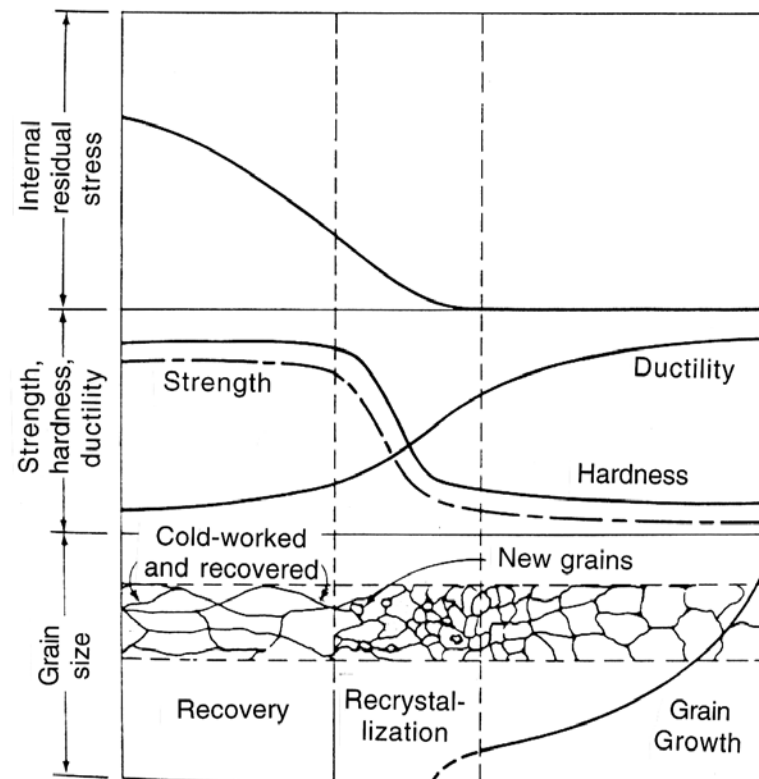
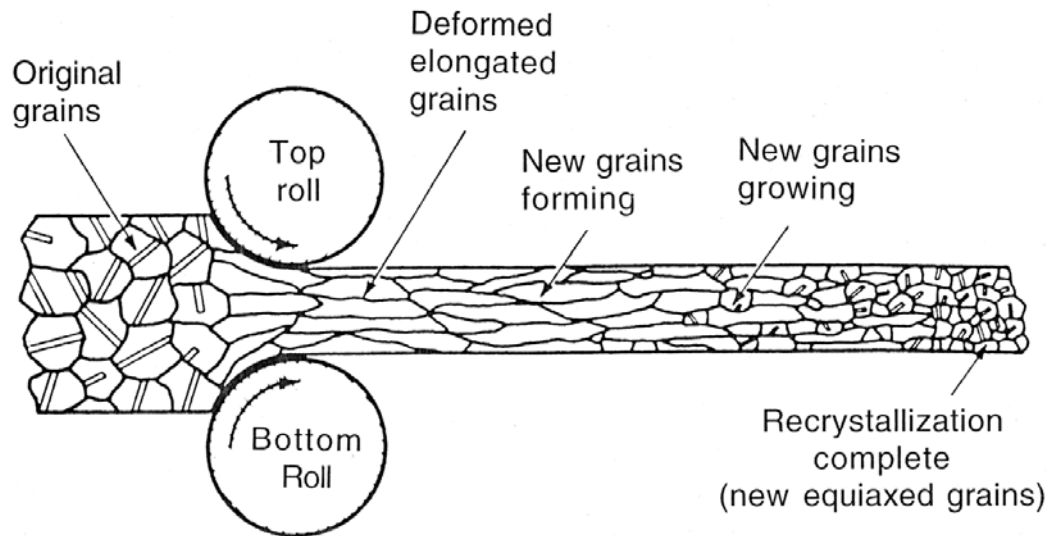


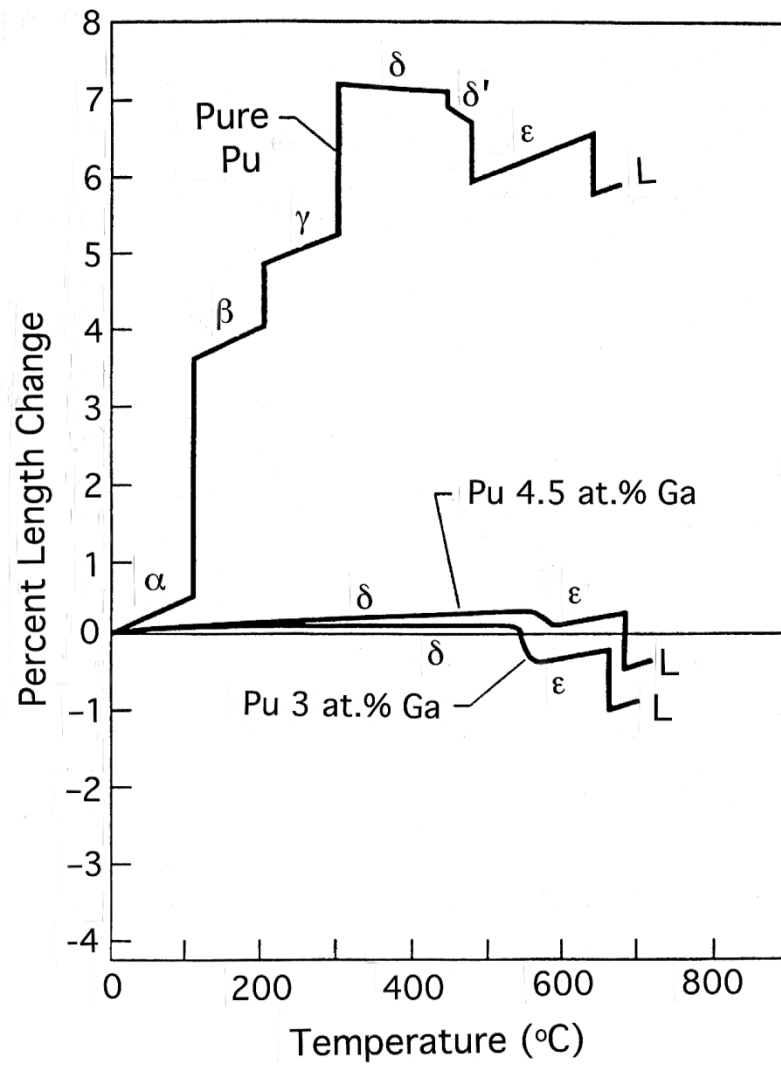
Homogenization ↓ at 450°C



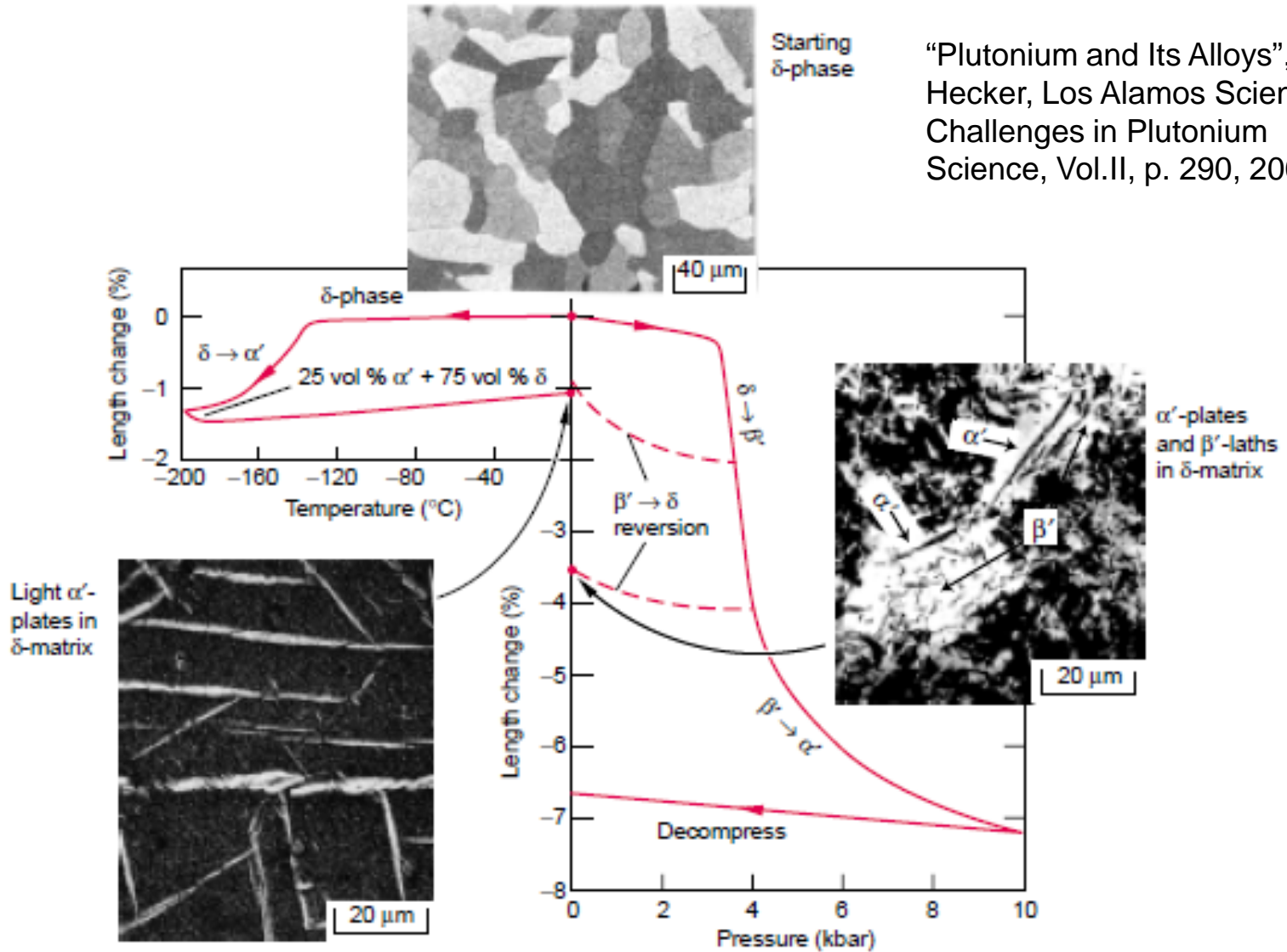
The Homogenized Pu-Ga Alloy is a Single Phase FCC Alloy







“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!