Title: Plutonium Metallurgy

Author(s): Freibert, Franz J.

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Plutonium Metallurgy

Franz Freibert, MST-16
Nuclear Materials Science Group

Los Alamos National Laboratory
Los Alamos, NM
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Reference Materials:


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


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


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


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

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,


Miscellaneous Report Archive Websites:
http://lasearch.lanl.gov/oppie/service - LANL Research Library Reports


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

Plutonium: Materials Science and Technological Uses
# Plutonium Applications

All stem from special nuclear properties of Pu

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{239}\text{Pu}$ Metal</td>
<td>Nuclear weapons, Early nuclear reactors</td>
</tr>
<tr>
<td>$^{239}\text{Pu}$ Oxide</td>
<td>Nuclear reactors, Mixed oxide fuels $^{238}\text{UO}_2$-$20%^{239}\text{PuO}_2$</td>
</tr>
<tr>
<td>$^{238}\text{Pu}$ Oxide</td>
<td>Radioisotope heat sources, Fuel for space power systems</td>
</tr>
</tbody>
</table>
Established Manufacturing Process
Known performance and margin based on well-known causal relationship between processing specifications and resultant structure, properties, and performance.

Specifications

Processing

Structure

Properties

Performance

(System Response, Corrosion Resistance, Density Stability, etc.)

(Mechanical, Thermodynamic, etc.)

Processing (Component Manufacturing)

Structure (From Microscopic to Macroscopic)

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

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.
The General Relationship of Material Structure Size in Determining Various Properties

STRUCTURE

Sub-atomic  Atomic  Phases  Micro  Macro

Nuclear  Electrical  Chemical  Thermal  Mechanical

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

L. J. Wittenberg and D. Otte*

Monsanto Research Corporation, Mound Laboratory,† Miamisburg, Ohio

and

C. F. Curtiss

Theoretical Chemistry Institute, University of Wisconsin, Madison, Wisconsin

(Received 18 January 1967)
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.

\[ \eta^{-1} = \frac{(V_i - c)}{B} = \frac{(V_i/B) - (c/B)}{B} \]

\[ \Delta V_f = (V_i - c) \]

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

\[ \frac{dT}{dP} = \frac{\Delta V_f}{\Delta S} \]
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 1968

FIG. 13. U-Pu-O ternary section at 400, 600 and 800°C.
MAMOX: Precursor Oxide Particle Morphology and Fuels Microstructure

DUO₂  11,000x

HEUO₂  1,400x

PuO₂  3,500x

NpO₂  2,300x

AmO₂  4,000x

Pressing and Sintering

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

Daughter Product Ingrowth in Weapons Grade Pu
Radioactive Decay of Plutonium

**Uranium:** Energy Deposition: Significant (85keV into 72,000 Unit Cells ~ 1.2meV/Å³)
Residual Defect Structures: vacancies and interstitials
Inclusion Phases?: U complexes, Solute-Solvent Complexes (δ-phase alloys)

**Alpha Particle:** Energy Deposition: Minimal (5Mev into 40x10¹² Unit Cells ~ 1.3neV/Å³);
Residual Defect Structures: not likely
Inclusion Phases: He Bubbles
Perspective: Atoms to Bulk

Relative Dimensions

- 0.5 - 3 Å: Atom
  - Type of Defect: Electron, $p^+$, $n^-$

- 3+ - 5 Å: Unit Cell
  - Type of Defect: Point Vacancy

- 10's - ~10^4 Å: Grains
  - Type of Defect: Line & Plane Dislocations, Faults, Boundaries

- 10^2 Å - very large: Bulk
  - Type of Defect: Volume Voids, Bubbles, Inclusions

- Flaws, “Cracks”

- Process
Plutonium Aging: Length Scales and Properties

Atomic scale ~ 10 Å
- atomic structure

Nanoscale ~ 100 Å
- nano structure

Microscale ~ 100 µm
- bulk properties
- lattice damage
- void swelling / He ingrowth
- He bubble formation
- Ga distribution “Coring”
- elastic properties
- density changes
- grain size
- dislocation structure

Macroscale ~ 100 cm
- component processes
- mechanical behavior
- dynamic properties
- stress-strain response
- strength, embrittlement
- weld stability
- corrosion behavior
- spall strength
- dimensional stability

Fundamental structure of homogeneous materials

Bulk properties of average structures, and heterogeneous materials

Controlling effects of heterogeneities, process coupling (chem, phys, mech)
Effects of Alpha Particle Decay Branch

Nanoscale:
- Atomic He insoluble $\rightarrow$ He atoms coalesce $\rightarrow$ 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

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 δ→α’ 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.
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: $-130^\circ\text{C}$.

Full reversion ($\alpha' \rightarrow \delta$) occurs from $-150$ to $150^\circ\text{C}$. Later thermal cycling shows:

- thermally induced swelling due to He bubble growth on heating; but
- typical $\delta$-phase thermal expansion on cooling.

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

![Graph showing thermal expansion of 7.5% $^{238}\text{Pu}$ alloy at 9 DPA](Freibert, 2008)

- Cool from $30^\circ\text{C}$ to $-150^\circ\text{C}$, 1 hr. Hold
- Heat from $-150^\circ\text{C}$ to $375^\circ\text{C}$
- Cool from $375^\circ\text{C}$ to $-150^\circ\text{C}$, 1 hr. Hold
- Heat from $-150^\circ\text{C}$ to $375^\circ\text{C}$
- Cool from $375^\circ\text{C}$ to $-150^\circ\text{C}$

$2.0$ at% Pu-Ga Alloy (9 DPA)
$\rho = 15.63\ \text{g/cm}^3$

- Cool from $30^\circ\text{C}$ to $-150^\circ\text{C}$, 1 hr. Hold
- Heat from $-150^\circ\text{C}$ to $375^\circ\text{C}$
- Cool from $375^\circ\text{C}$ to $-150^\circ\text{C}$, 1 hr. Hold
- Heat from $-150^\circ\text{C}$ to $375^\circ\text{C}$
- Cool from $375^\circ\text{C}$ to $-150^\circ\text{C}$
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
<table>
<thead>
<tr>
<th>Phase</th>
<th>Stability Range °C</th>
<th>Space Lattice and Space Group</th>
<th>Unit Cell Dimensions, Å</th>
<th>Atoms per unit Cell</th>
<th>X-ray Density, gm/cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>Below ~115</td>
<td>Simple monoclinic $P2_1/m$</td>
<td>@21°C:</td>
<td>16</td>
<td>19.86</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>a= 6.183 ±0.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>b= 4.822 ±0.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>c= 10.963 ±0.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>β= 101.79° ±0.01°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>β</td>
<td><del>115</del>200</td>
<td>Body-centered Monoclinic $I2/m$</td>
<td>@190°C:</td>
<td>34</td>
<td>17.70</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>a= 9.284 ±0.003</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>b= 10.463 ±0.004</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>c= 7.859 ±0.003</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>β= 92.13° ±0.03°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>γ</td>
<td>~200-310</td>
<td>Face-centered orthorhombic $Fdd$</td>
<td>@235°C:</td>
<td>8</td>
<td>17.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>a= 3.159 ±0.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>b= 5.768 ±0.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>c= 10.162 ±0.002</td>
<td></td>
<td></td>
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<tr>
<td>δ</td>
<td>310-452</td>
<td>Face-centered cubic, $Fm3m$</td>
<td>@320°C:</td>
<td>4</td>
<td>15.92</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>a= 4.6371 ±0.004</td>
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<tr>
<td>δ'</td>
<td>452-480</td>
<td>Body-centered tetragonal $I4/mmm$</td>
<td>@465°C:</td>
<td>2</td>
<td>16.00</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>a= 3.34 ±0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>c= 4.44 ±0.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ε</td>
<td>480-640</td>
<td>Body-centered cubic, $Im3m$</td>
<td>@490°C:</td>
<td>2</td>
<td>16.51</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>a= 3.6361 ±0.004</td>
<td></td>
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</tr>
</tbody>
</table>
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: \(\alpha'\))

- **Ga Alloying**
  Lowers \(\delta\)-Pu Phase Free Energy and Stabilizes \(\delta\)-Pu
  Substitutional in \(\delta\)-Pu (XAFS)
  Alters Electronic Structure (TEC - \(\rightarrow\) +)
  Diffusional \(\delta\leftrightarrow\varepsilon\) transformation

- **Impact of Microstructure and Impurities**
  Grain size, Morphology, and Texture
  \(\text{Pu}_6\text{Fe}\) and other Inclusions

- **Anharmonic Effects**
  Non-Debye Solid Behavior
Unalloyed \( \delta \)-Pu and 2at% Ga stabilized \( \delta \)-Pu are elastically similar!

- Unalloyed and Ga alloyed \( \delta \)-Pu exhibit same values of bulk and shear elastic moduli:
  
  \[
  \begin{align*}
  B_{\delta-Pu} &= 20.6 \text{ GPa} \\
  G_{\delta-Pu} &= 11.8 \text{ GPa} \\
  B_{\delta-PuGa}^{\text{Ext.}} &= 22 \text{ GPa} \\
  G_{\delta-PuGa}^{\text{Ext.}} &= 12 \text{ GPa}
  \end{align*}
  \]

- \( \alpha \rightarrow \beta \), \( \beta \rightarrow \gamma \), and \( \gamma \rightarrow \delta \) Pu transformation are continuous.

- \( \beta \)-Pu and \( \gamma \)-Pu exhibit the same shear modulus with a 30% variation in bulk modulus.
The diagram illustrates the relationship between stress, strain, and temperature in the context of material properties, specifically for Plutonium. The graph on the right shows the stress-strain relationship at various temperatures, with different phases identified: Alpha, Beta, Gamma, and Delta. The graph includes symbols and annotations indicating testing conditions and material states.

Key equations and definitions:

- \( \sigma = \frac{\text{Load}}{\text{Area}} \)
- \( \sigma = E\varepsilon \) (Hook's Law)
- \( \sigma_y = \text{Yield Stress} \)
- \( E = \text{Modulus of Elasticity} \)
- \( \mu = \text{Poisson's Ratio} \)
- \( E = 2(1+\mu)G \)
- \( G = \text{Shear Modulus} \)
Plutonium Alloys and Metallurgy
<table>
<thead>
<tr>
<th>Phase</th>
<th>To R.T.</th>
<th>Not to R.T. (&gt;1 wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>Np, Ru, Zr</td>
<td></td>
</tr>
<tr>
<td>β</td>
<td></td>
<td>Np, U, Zr</td>
</tr>
<tr>
<td>γ</td>
<td></td>
<td>Np, Th, U, Zr</td>
</tr>
<tr>
<td>δ</td>
<td>Al, Am, Ce, Ga, Sc</td>
<td>In, Np, Nd, Pm, Ru, Si, Sm, Th, Ti, U, Zn, Zr</td>
</tr>
<tr>
<td>δ'</td>
<td></td>
<td>Am, Np</td>
</tr>
<tr>
<td>ε</td>
<td></td>
<td>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</td>
</tr>
</tbody>
</table>
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.
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.
Solidification within $\varepsilon+L$ phase field involves equiaxed dendrite formation initiated at the mold walls. Microsegregation of Ga or “coring” occurs.

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

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

Phase segregation occurs in Pu rich regions. Upon cooling, $\alpha$-phase regions contain soluble Ga. Both $\alpha$-phase and $\delta$–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 $\delta$ Cores Surrounded by Light Low-Gallium $\alpha$ Matrix
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

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Homogenization at 450\(^0\)C

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50 \(\mu\)m Grain

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24 hours
The Homogenized Pu-Ga Alloy is a Single Phase FCC Alloy
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!