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INL

Composition-Dependent Growth Kinetics of Intermetallic Phases in U-Mo vs. Al Alloy Diffusion Couples Annealed at 550º and 600ºC

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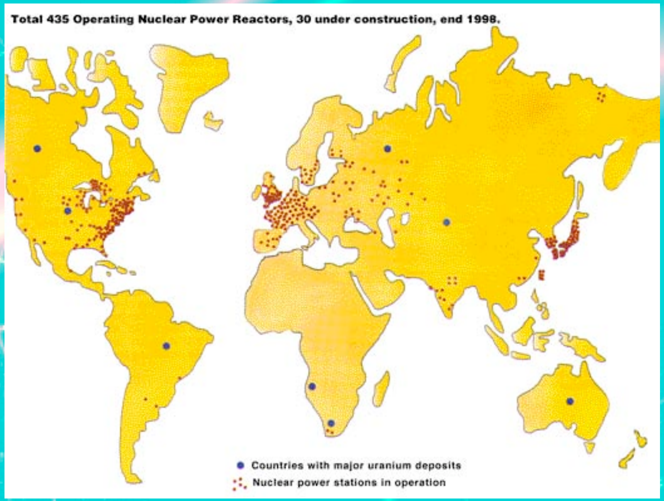
Nuclear Energy

- Nuclear reactors will play a larger role for generating energy:
  - ✓ Currently 104 reactors provide ~20% of electricity in U.S.
    - → This equals what is used by California, Texas, and New York.
    - → Over 430 reactors worldwide (provides 17% of electricity).
  - ✓ Help to reduce emissions of greenhouse gases.



Total 435 Operating Nuclear Power Reactors, 30 under construction, end 1998.

● Countries with major uranium deposits

⁛ Nuclear power stations in operation

- Currently, more advanced reactors are being developed for a variety of applications:
  - ✓ GEN IV reactors are being developed to provide energy efficiently, cost-effectively, and with minimal waste generation.
  - ✓ NGNP is being developed to provide process heat to support hydrogen production.
  - ✓ Space reactors are being developed to power space craft and provide power at remote space locations (e.g., Mars).

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Nuclear Energy and Advanced Fuels

- To support development of these different types of reactors, need fuels that will withstand more aggressive reactor conditions.
  - ✓ This includes higher temperatures, higher burn-ups (heavy metals fissioned), etc.
- Many types of fuel materials are being investigated:
  - ✓ Ceramics, metallic alloys, molten salts, ceramic-ceramic composites, metal-matrix composites, etc.
- Fuel Performance and Challenges:
  - ✓ Swelling: The accumulation of two fission product atoms for each atom fissioned. This is aggravated by the fact that some of the fission products are gases.
  - ✓ Melting
  - ✓ Thermal conductivity / Thermotransport
  - ✓ Fuel restructuring
  - ✓ Fuel/Cladding Interaction (FCI)

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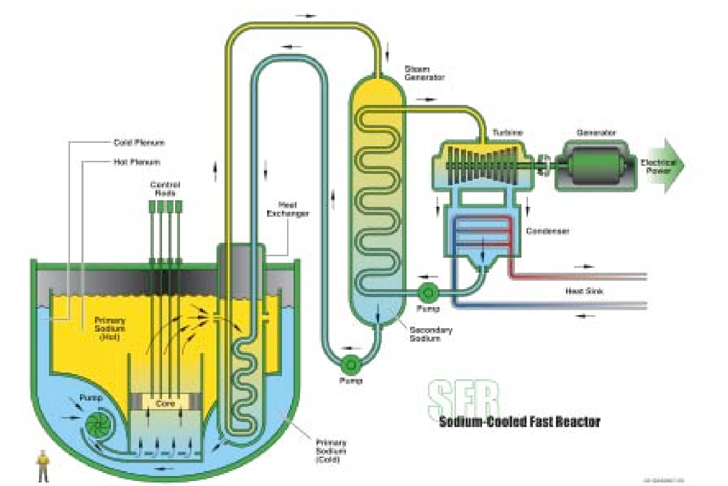
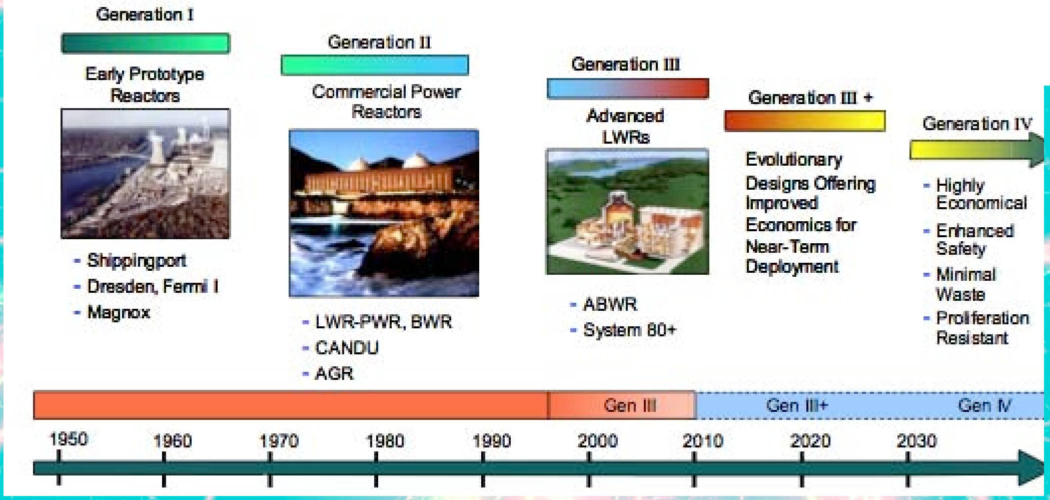
Generation IV Reactors

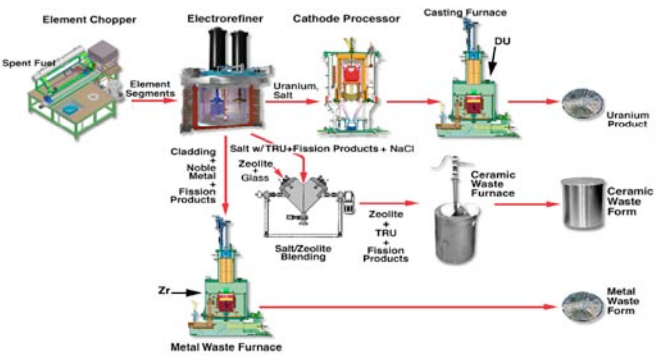
- **Six reactor concepts are being evaluated.**
  - ✓ **Lead-cooled fast reactor**
  - ✓ **Molten salt reactor**
  - ✓ **Sodium-cooled fast reactor**
  - ✓ **Supercritical water cooled reactor**
  - ✓ **Gas Fast Reactor**
  - ✓ **High Temperature Gas Reactor**





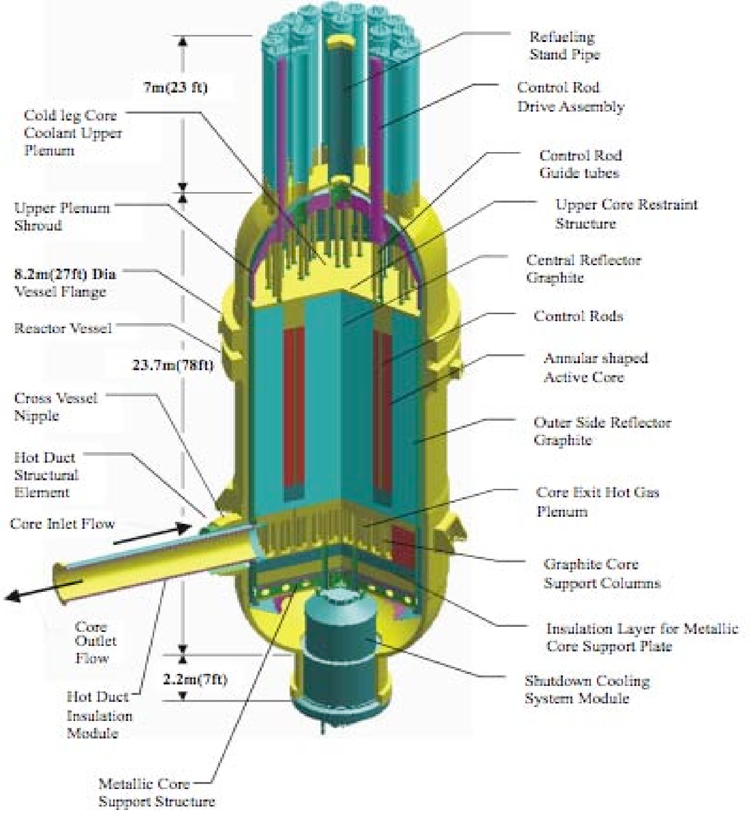
Sodium fast reactors can utilize almost all the energy in natural uranium versus the 1% utilized in thermal spectrum systems.

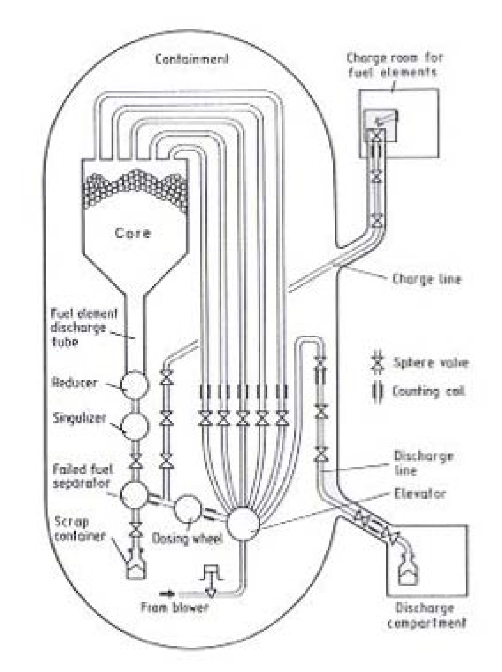
Pyrochemical processing to minimize waste products.



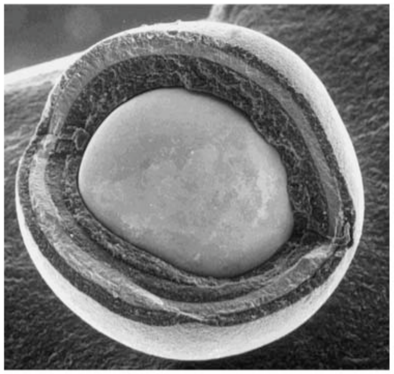
Next Generation Nuclear Plant (NGNP)

- Prismatic block design or pebble bed design.
- Uses He coolant.
- Refractory coated fuel.
- Graphite moderator
  - ✓ High temperature stability.
- Provide process heat to supply a hydrogen production plant.





Pebble Bed Design



- 360,000 “pebbles” in core.
  - ✓ 350 discharged daily.
  - ✓ One pebble discharged every 30 seconds.
  - ✓ Average pebble cycles through core 15 times.

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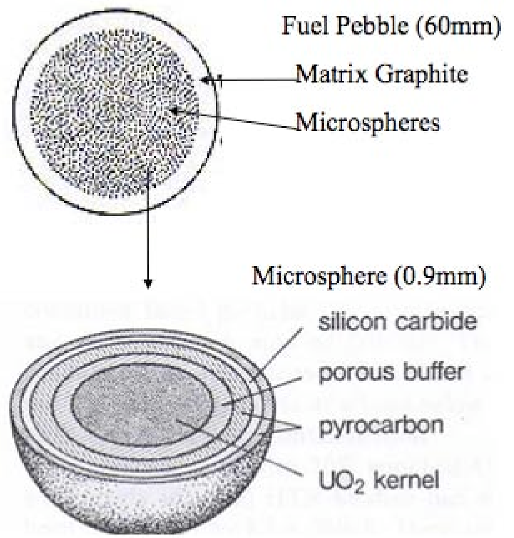
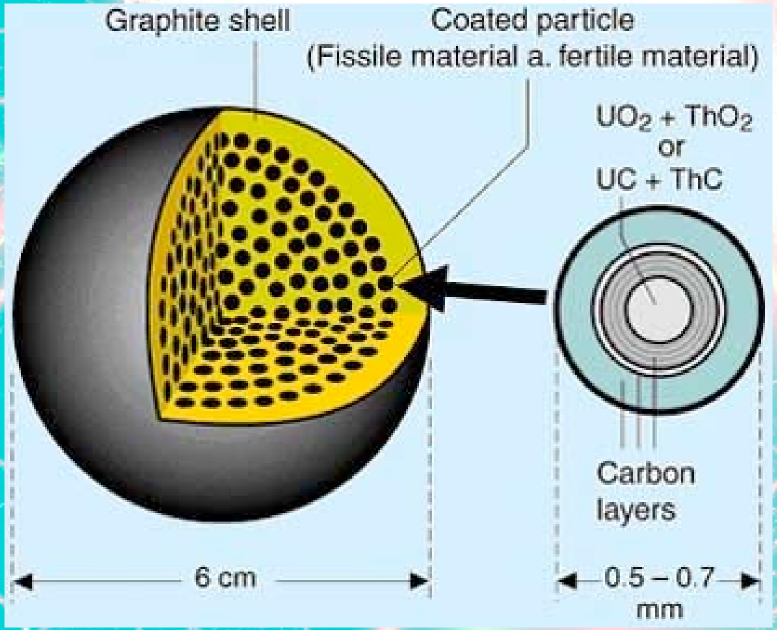
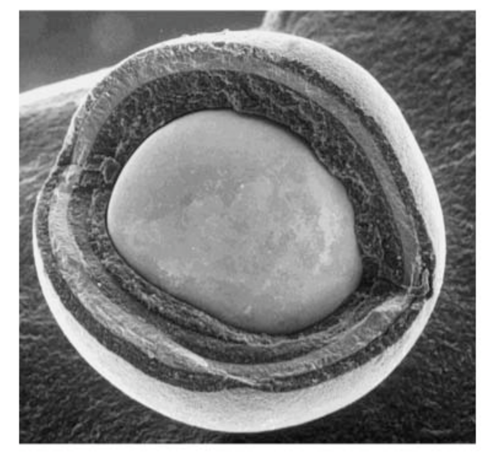
NGNP Fuel Particle in Pebble Bed Design







- The layers that surround fuel kernel include an inner pyrolytic carbon (IPyC) layer, a SiC layer, and an outer pyrocarbon (OPyC) layers.
  - Layers act as pressure vessel for fission product gases.
  - Barrier to migration of other fission products.

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Space Reactors

- Radio-isotope Thermal Generator (RTG) employed for “New Horizons” mission to Pluto.
  - ✓ Use natural decay of Pu238 to provide heat and electricity.
- Ultimately reactors will be used to provide energy in space.

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Generation IV Reactor Fuel and Cladding

- Experimental Breeder Reactor-I (EBR-I) and EBR-II were successfully operated using metallic fuels (at INL).
  - The fuels used were primarily U-base (e.g., U-Zr, U-Pu-Zr) alloys.
  - The reactors demonstrated a high degree of safety, a compact design, and relatively small amounts of waste generation.

- The maximum fuel operating temperature allowed for a fuel/cladding interface temperature of 650°C.

- Multicomponent, multiphase diffusion is commonly observed in irradiated metallic nuclear fuels.
  - This diffusion occurs in the presence of temperature gradients, power gradients, the generation of fission products, fission density gradients, etc.
  - The resulting phases that form affect the performance of irradiated nuclear fuels.

- Eventually the fuel will swell and contact the cladding.
  - Interdiffusion occurs between the constituents in the cladding and fuel, along with generated fission products.

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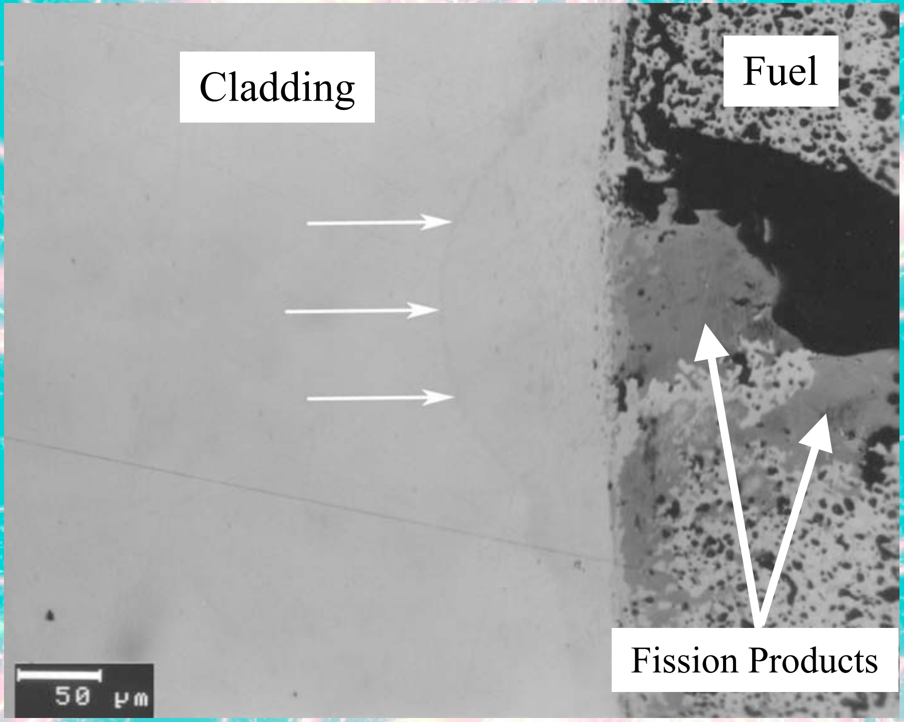
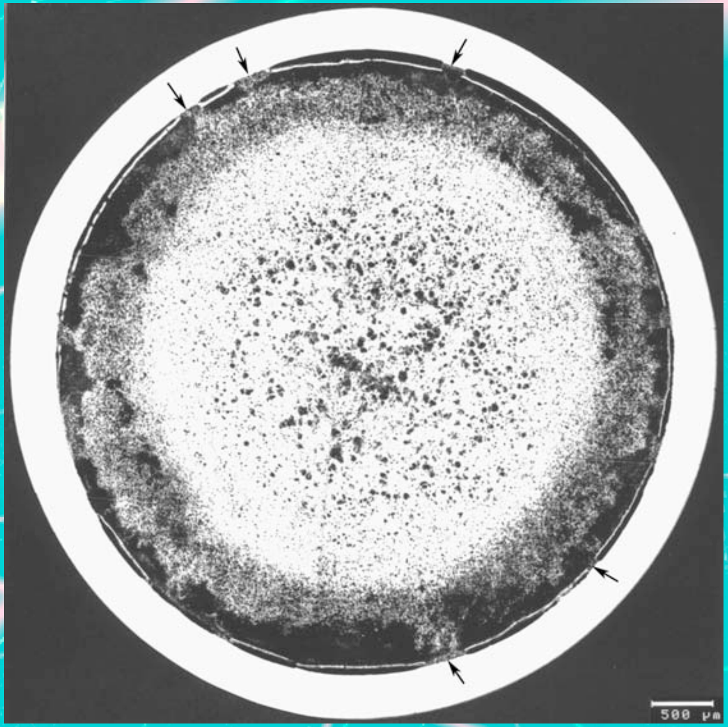
Example of Fuel/Cladding Interaction in An Irradiated U-Pu-Zr Alloy Fuel





U-16Pu-23Zr, D9 cladding, 11.3 at% Burnup

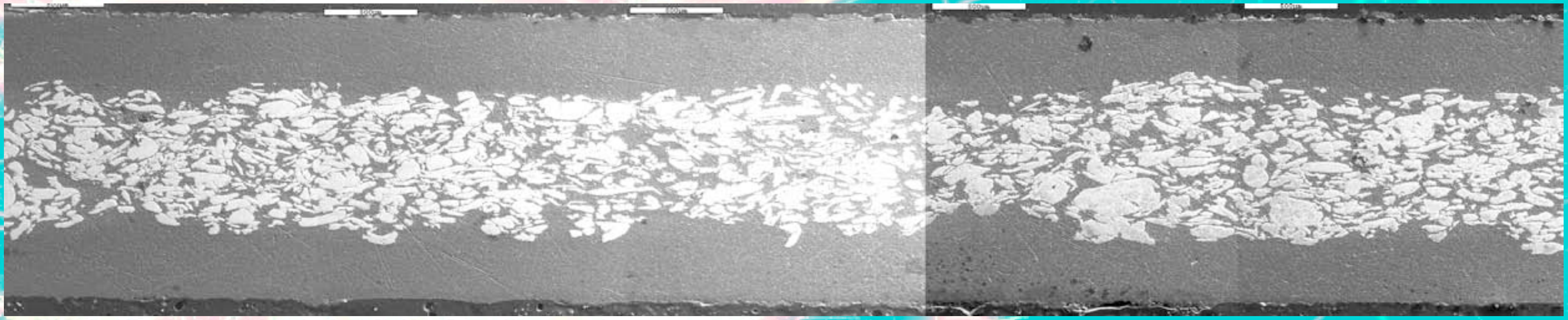
Swelling and interdiffusion between the fuel and cladding alloy constituents results in the formation of reaction zones at the inner surface of the cladding. These zones are brittle and can form cracks.

Further Consideration in Fuel Development: Low-Enriched Uranium-base Fuels

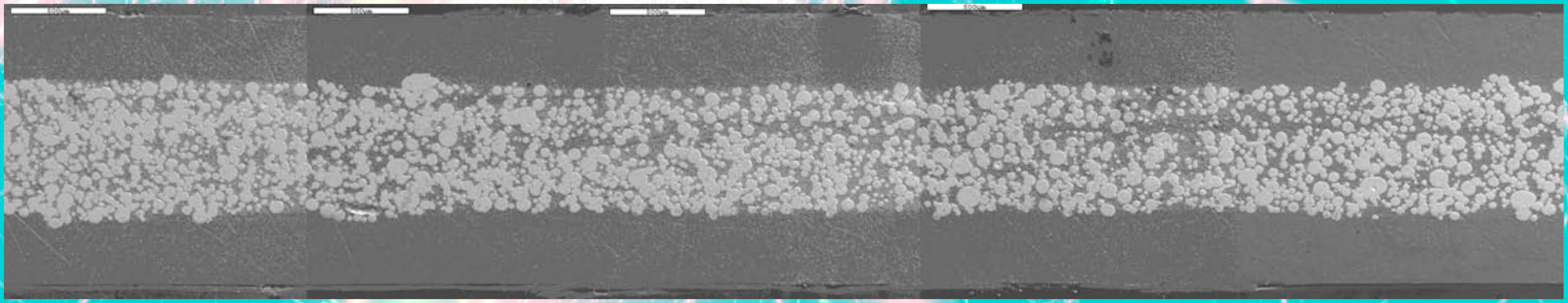
Reactor performance

Economics

Safety / Security



Machined U-10Mo, ~8 g-U/cm^3



Atomized U-10Mo, ~8 g-U/cm^3

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Further Consideration in Fuel Development: Low-Enriched Uranium-base Fuels

- Dispersion Fuel Fabrication Process:
  - ✓ Fuel powder production (powder size 20 to 125µm)
    - ➔ Grinding/Machining/Communition (ANL, AECL)
    - ➔ Atomization (KAERI)
  - ✓ Fuel-matrix powder blending
  - ✓ Press fuel-matrix blend into a compact
  - ✓ Insert compact into aluminum frame and weld to assemble
  - ✓ Hot roll assembly to final thickness, ~1.25-mm
  - ✓ Blister anneal to verify aluminum bonding
  - ✓ Radiograph to locate fuel zone
  - ✓ Shear to final plate length and width

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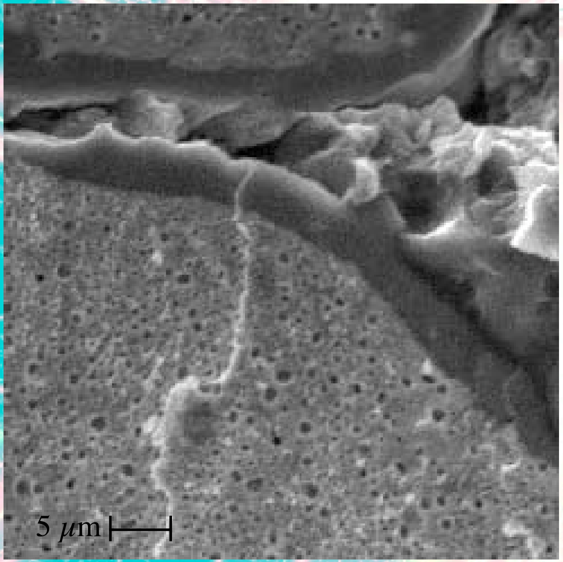
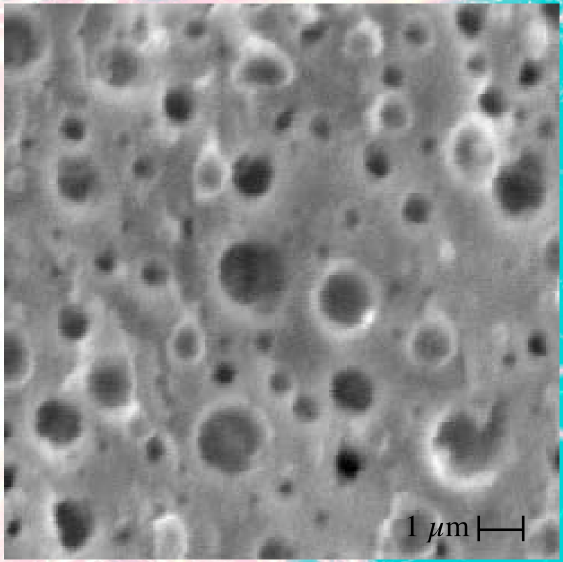
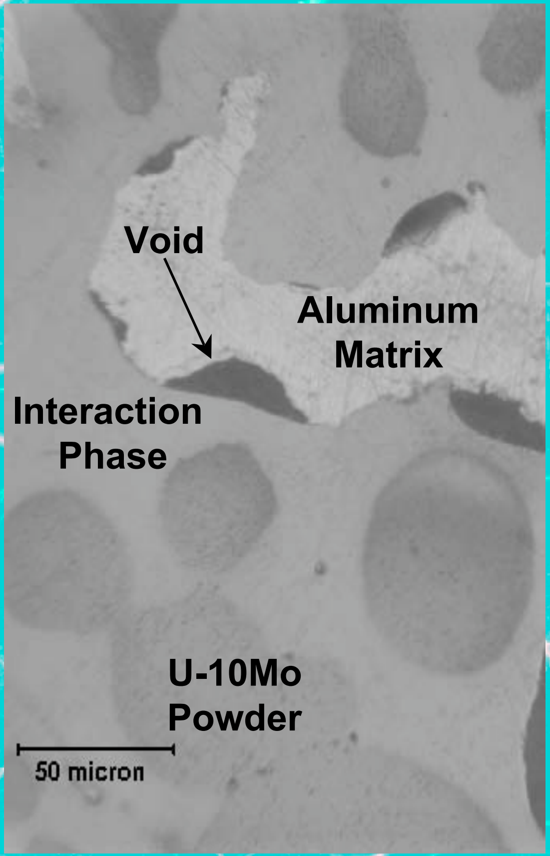
Low-Enriched Uranium-base Fuels: U-Mo Alloys

- U-10Mo fuel irradiated in RERTR-2
  - ✓ Low temperature, < 100°C
  - ✓ High burnup, 70% U^{235}







- Interaction of fuel and cladding in irradiated fuel produces phases that can potentially contribute to swelling of fuel plates:
  - Al-rich phase $(U,Mo)Al_x$ may contribute to increased swelling.

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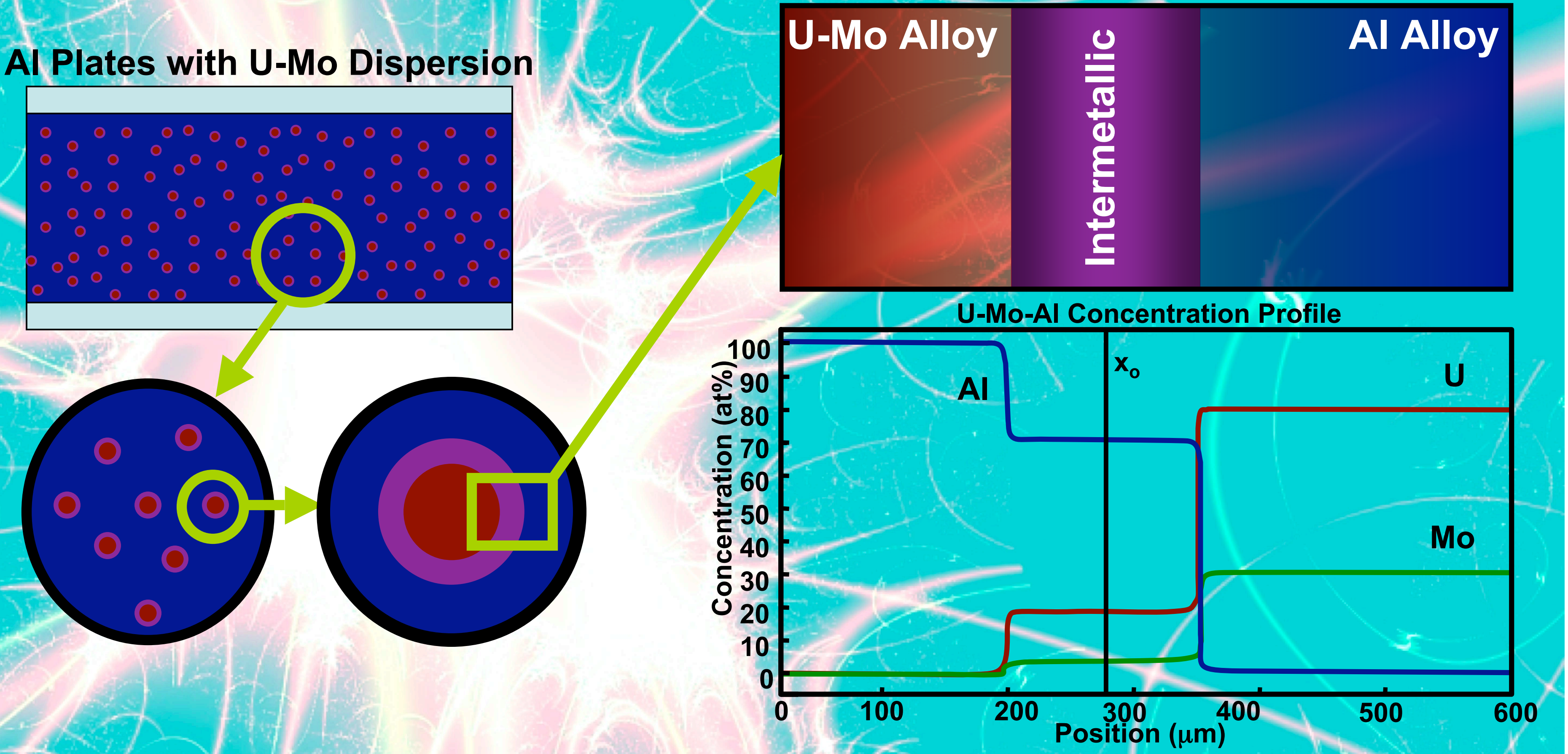
Interdiffusion in U-Mo/Al Dispersions Fuels



- U-Mo/Al dispersion fuels form an undesired intermetallic layer with low thermal conductivity that is a result of interdiffusion between the fuel and the Al matrix.
  - ✓ The growth of this layer must be minimized or eliminated.
- Layer growth can be controlled by reduction of the interdiffusion flux by compositional modification or alloy additions of the system according to:

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Objectives

- To examine the growth and composition of the intermetallic compound layers that develop in U-Mo/Al system to improve the performance and service life of U-Mo/Al dispersion fuels.
- Examine the interdiffusion behavior between U-Mo alloys and Al-alloys with specific Si alloying additions.
- Findings and understanding from this program will provide strategies and solutions to minimize the interdiffusion-induced degradation of U-Mo alloys.

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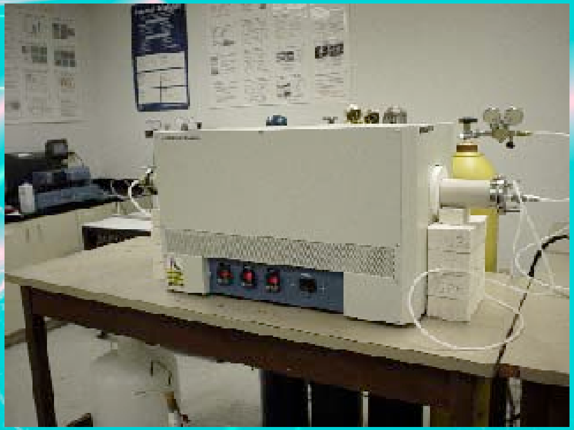
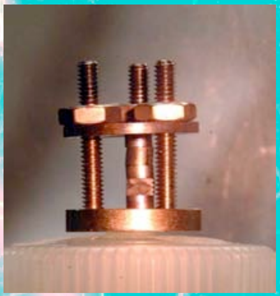
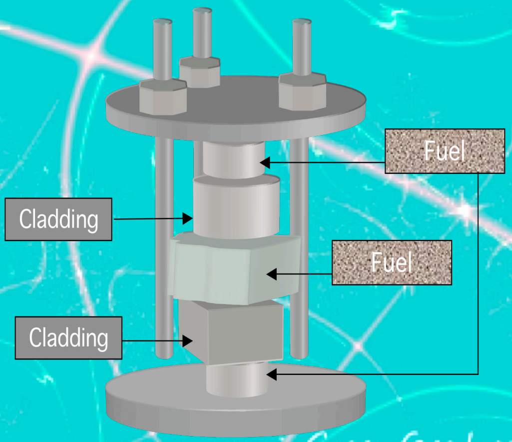
Experimental Details



- Solid-to-solid diffusion couple alloys were sectioned, polished and assembled under a controlled Ar atmosphere in a glove box.
- Diffusion couples were wrapped in Ta foil, and encapsulated in quartz capsule in Ar atmosphere after Argon flush for heat treatment.
- Diffusion anneal performed using a Lindberg/Blue 3-Zone horizontal tube furnace.
- Diffusion structures examined by optical and scanning electron microscopy.
- Concentration profiles determined by Electron Probe Microanalysis (EPMA) using pure standards and ZAF correction.





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Experimental Details

- Diffusion couples were assembled using U-7Mo, U-10Mo and U-12Mo with pure Al (99.999%), Al-2Si and Al-5Si (wt.%) and commercially available 4043Al and 6061Al alloys.
  - ✓ Alloys cast at INL (U-alloys) and ANL (Al-Si alloys).
  - ✓ Homogenization at UCF.
- The couples were heat-treated in Ar-atmosphere for 24 hours at 550°C and 600°C. Anneal at 500° and 300°C will be carried out.
- The Matano plane was approximated from experimental concentration profiles.
- The interdiffusion flux was calculated directly from the concentration profiles.
- The integrated interdiffusion coefficients have been determined for the major components.

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Interdiffusion Flux and Integrated Interdiffusion Coefficients

- **Interdiffusion fluxes of all components can be determined directly from their concentration profiles without the need of the interdiffusion coefficients:**

$$\tilde{J}_i = \frac{1}{2t}\int_{C_i^- \text{ or } C_i^+}^{C_i(x)} (x - x_o)\,dC_i \quad (i = 1, 2, .., n)$$

- **Integrated interdiffusion coefficients for a component *i* on either side of the Matano plane can be defined as:**

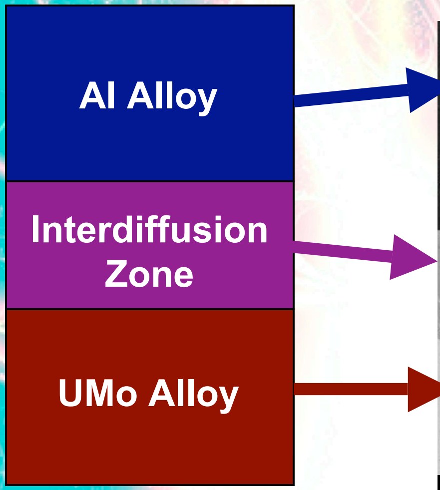
$$D_{i,L}^{int} = \int_{-\infty}^{x_o} \tilde{J}_i(x)\,dx \quad \text{and} \quad D_{i,R}^{int} = \int_{x_o}^{+\infty} \tilde{J}_i(x)\,dx$$

- **The Total Integrated interdiffusion coefficients for a component *i* over the entire concentration profile:**

$$D_{i,Tot}^{int} = \int_{-\infty}^{-\infty} \tilde{J}_i(x)\,dx$$

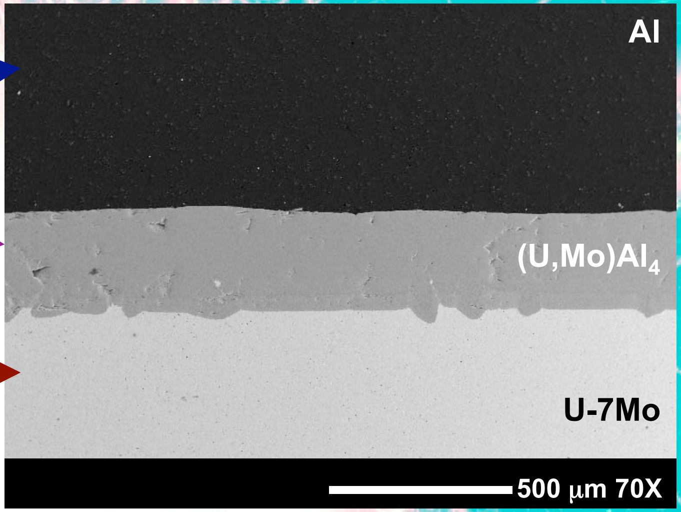
M. A. Dayananda, Y.H. Sohn, Scripta Mater., 35 (1996) 683.

Typical Microstructural Development

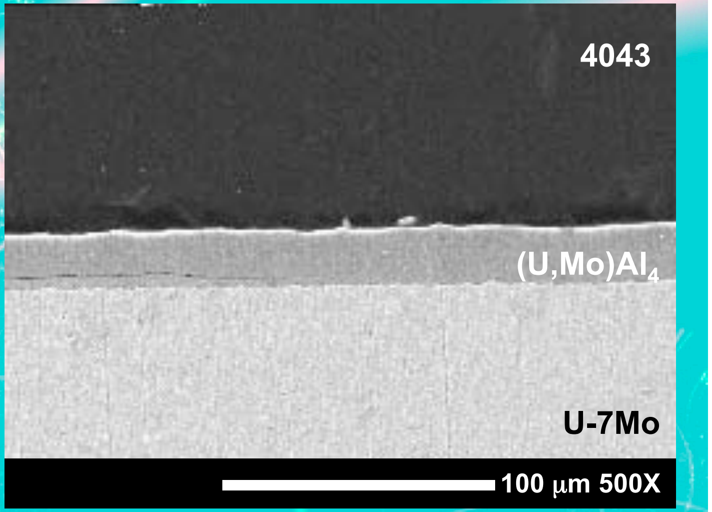


Typical layout for diffusion couple microstructural development after Heat Treatment.

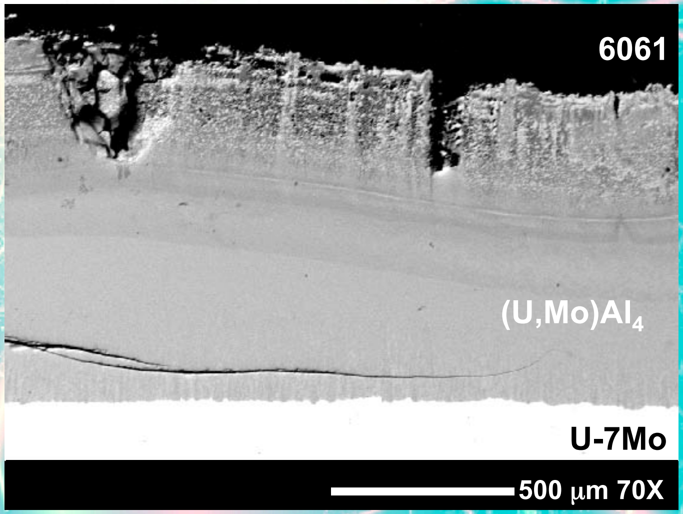
U-7Mo vs. Al (600°C for 24hr)



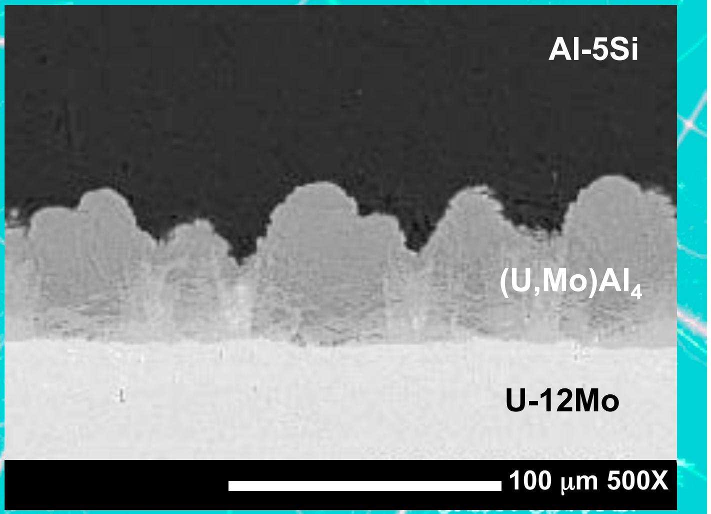
U-7Mo vs. 4043 (550°C for 24hr)



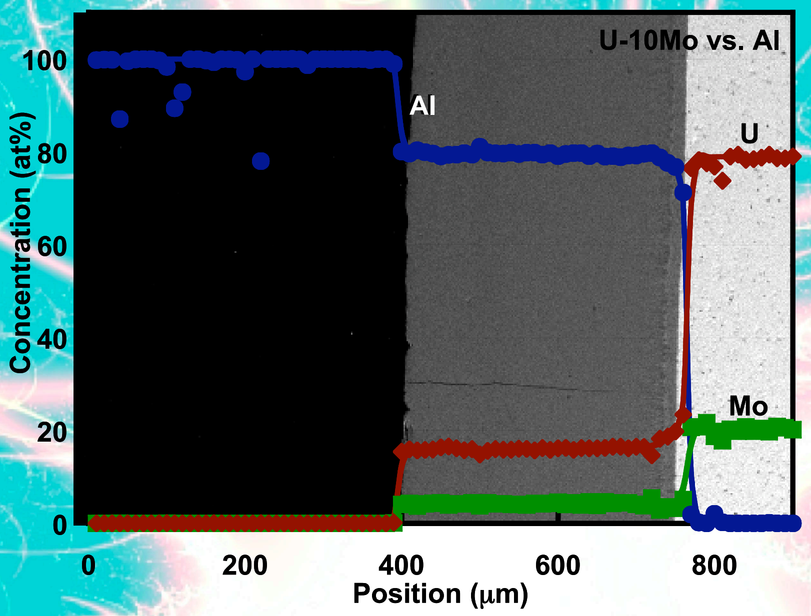
U-7Mo vs. 6061 (600°C for 24hr)

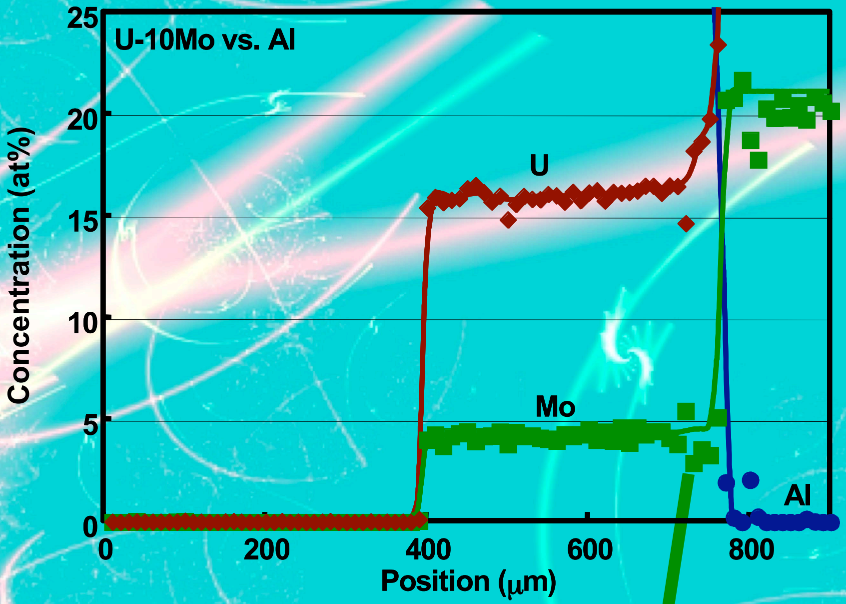


U-12Mo vs. Al-5Si (550°C for 24hr)

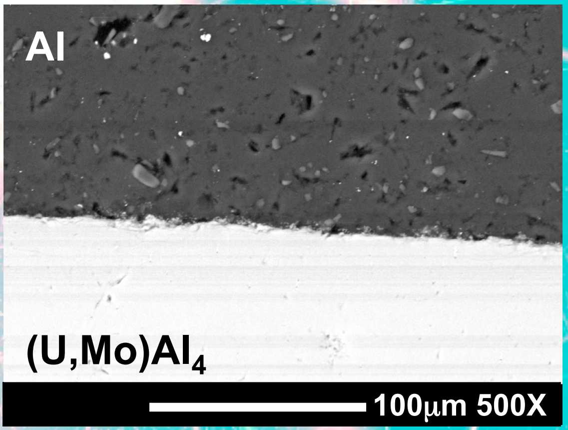


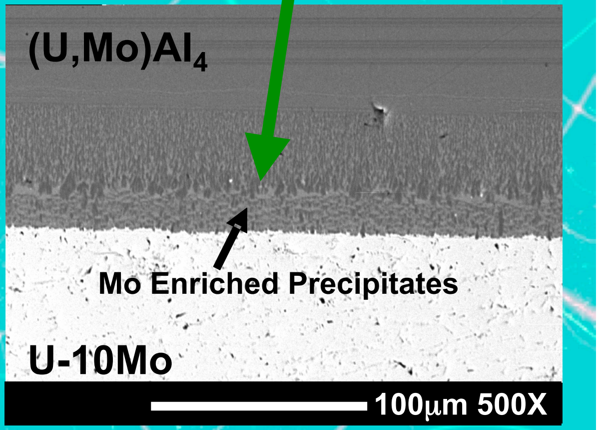
U-10Mo vs. Al Diffusion Couple (600°C for 24hr)





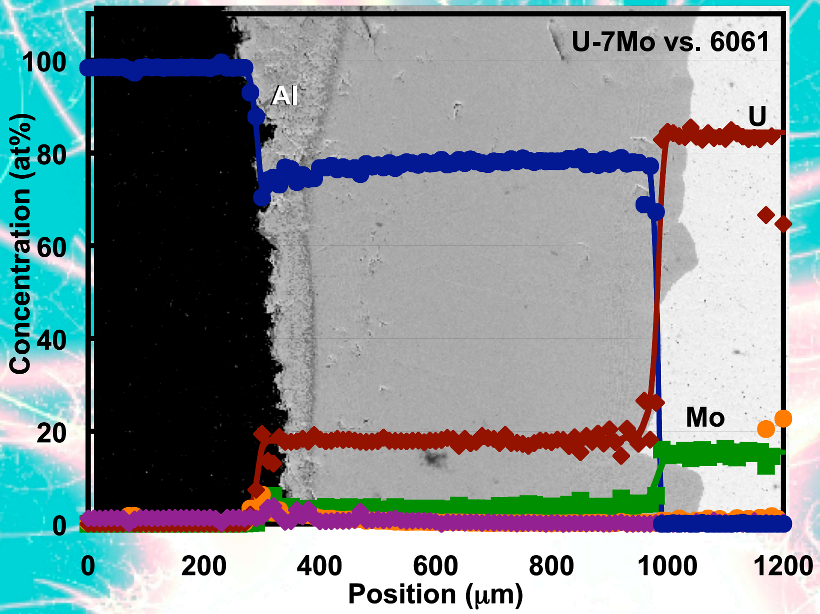
- The interdiffusion zone developed planar interfaces.
- The U-rich side of the interdiffusion zone developed an area with Mo rich precipitates.

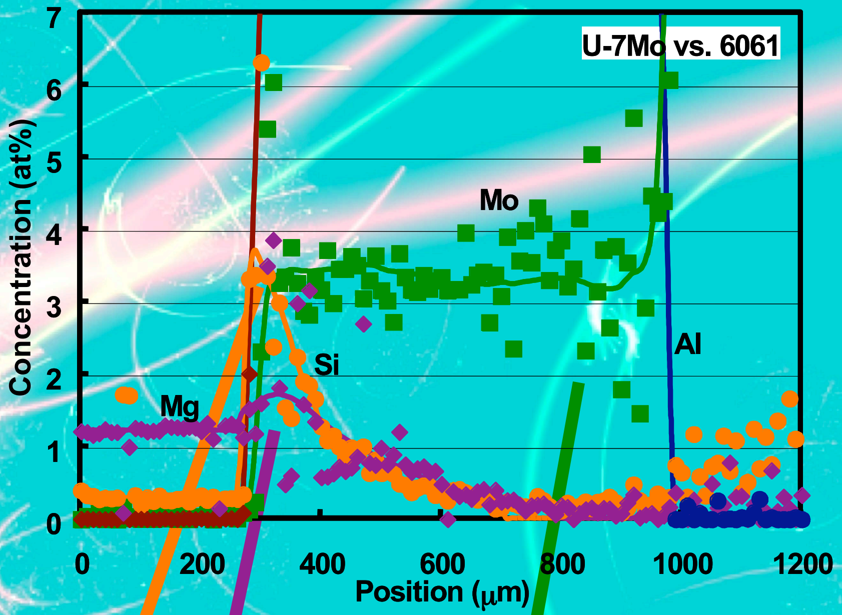




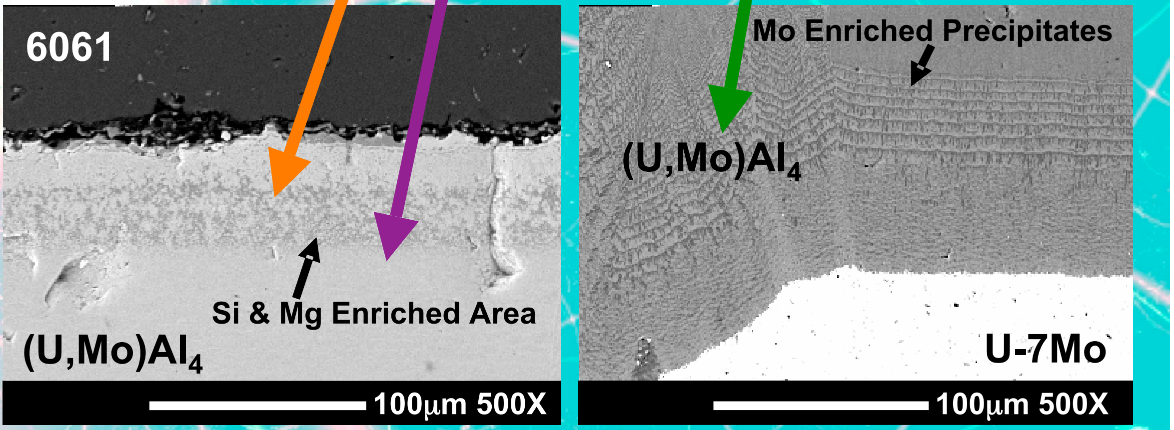
Majority of Intermetallic Layer: (U,Mo)Al_4

U-7Mo vs. 6061 Diffusion Couple (600°C for 24hr)



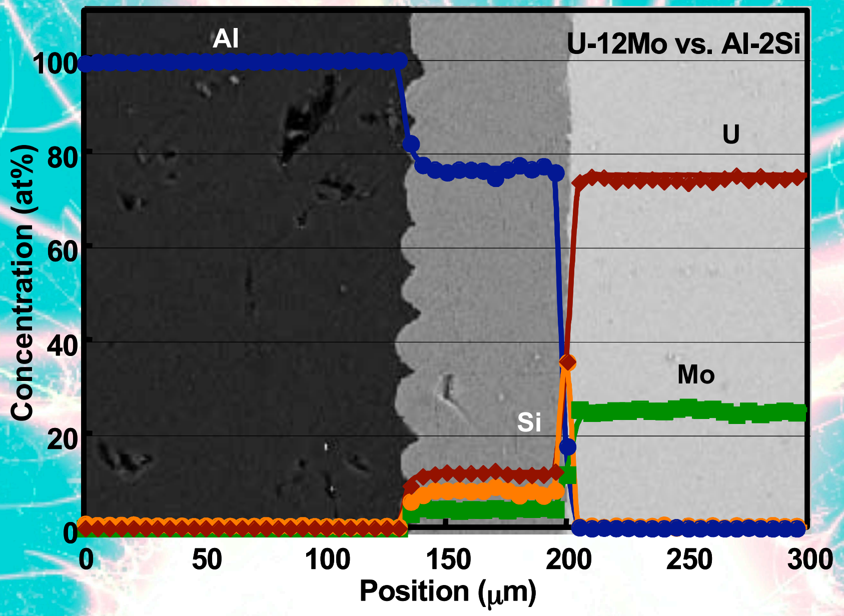


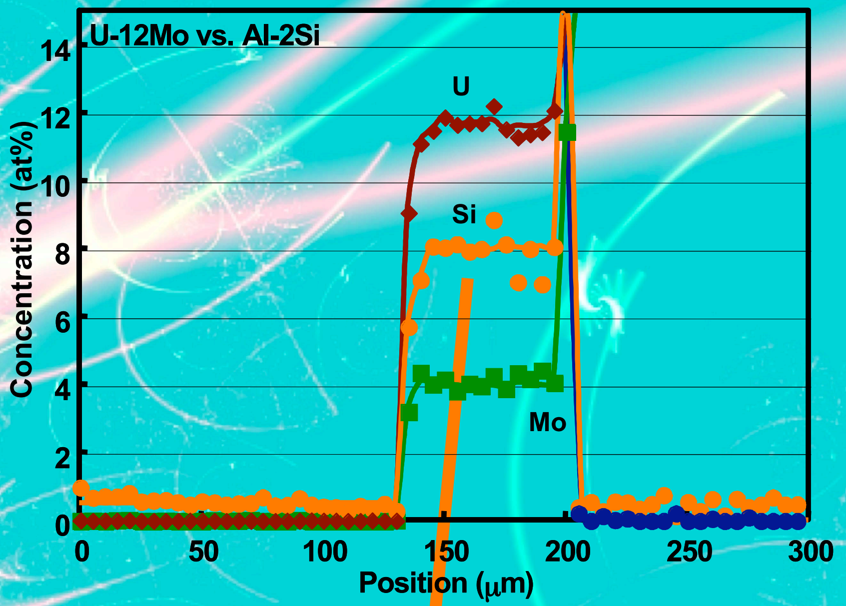
- Si and Mg-rich phases precipitated in the Al-rich side of the interdiffusion zone.
- The U-rich side of the interdiffusion zone developed an area with Mo rich precipitates.



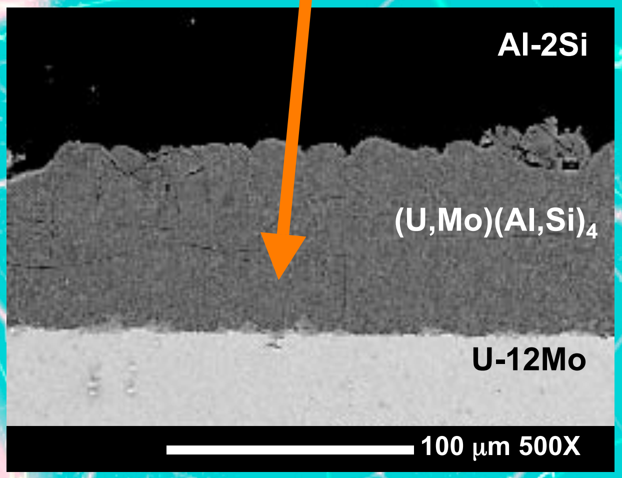
Majority of Intermetallic Layer: (U,Mo)Al_4

U-12Mo vs. Al-2Si Diffusion Couple (550°C for 24hr)





- Si containing diffusion couples developed interdiffusion zones rich in Si.
- The thickness of the interdiffusion zones was significantly reduced.
- The intermetallic phase maintained the $(U,Mo)(Al,Si)_4$ composition.



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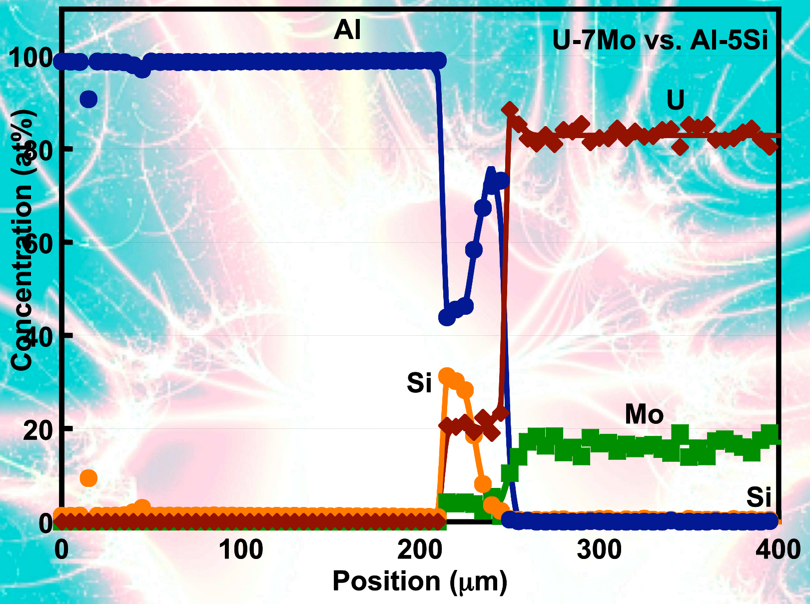
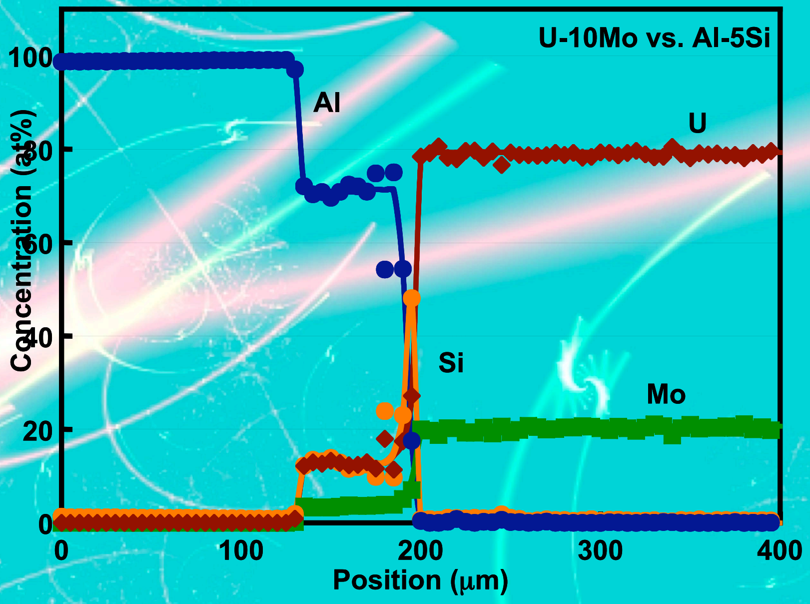
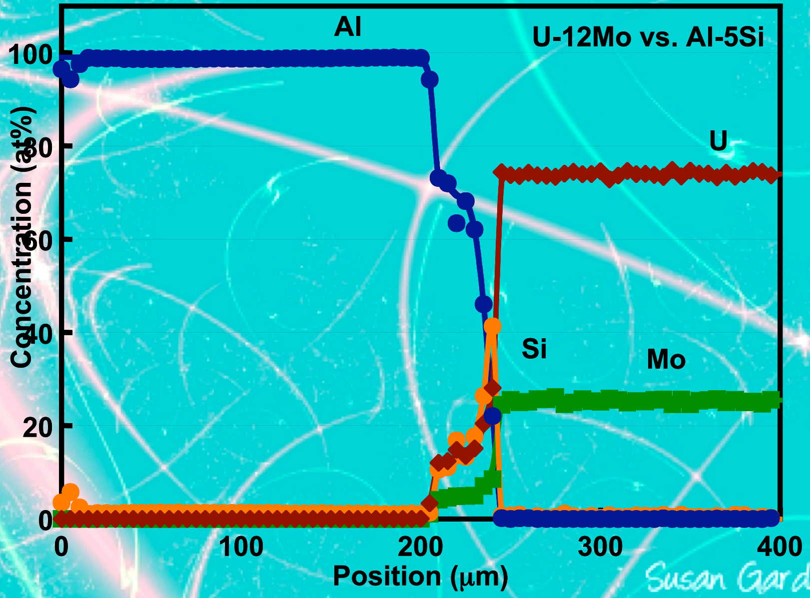
Observed Behavior of Si in the Interdiffusion Zone





- For diffusion couples with 4043, Al-2Si and Al-5Si Alloys:
  - ✓ Si build-up in the interdiffusion zone near the Al-alloy/Intermetallic interface for couples with U-7Mo alloys.
  - ✓ Si build-up in in the interdiffusion zone near U-Mo/Intermetallic interface for couples with U-10Mo and U-12Mo alloys.



Integrated Interdiffusion Coefficients

600°C for 24 Hours

Diffusion Couple	$\tilde{D}^{int}_{i,Tot}$ 10^{-14}		
	Al	*Mo*	*U*
U-7Mo vs. Al	5.97	-1.0	-4.9
U-7Mo vs. 6061Al	49.9	-7.4	-40.2
U-10Mo vs. Al	13.5	-2.8	-10.5
U-10Mo vs. 6061Al	161.0	-34.1	-126.0
U-12Mo vs. Al	3.48	-0.9	-2.53
U-12Mo vs. 6061Al	75.0	-6.16	-17.3

- Integrated interdiffusion coefficients offer a measure of the accumulated interdiffusion flux and its direction for a component in diffusion couples.

Diffusion coefficients in atf•m^2/sec.

550°C for 24 Hours

Diffusion Couple	$\tilde{D}^{int}_{i,Tot}$ 10^{-16}		
	Al	*Mo*	*U*
U-7Mo vs. Al	*	*	*
U-7Mo vs. 6061Al	3535.8	662.5	-4188.2
U-7Mo vs. 4043Al	4.6	-0.7	-2.7
U-7Mo vs. Al-2Si	7.1	-1.3	-5.5
U-7Mo vs. Al-5Si	27.5	-3.4	-12.4
U-10Mo vs. Al	*	*	*
U-10Mo vs. 6061Al	1473.3	-321.9	-1039.4
U-10Mo vs. 4043Al	*	*	*
U-10Mo vs. Al-2Si	*	*	*
U-10Mo vs. Al-5Si	56.0	-7.8	-29.7
U-12Mo vs. Al	1555.0	-419.4	-1106.5
U-12Mo vs. 6061Al	1004.1	-109.1	-321.2
U-12Mo vs. 4043Al	5.9	-1.9	-5.8
U-12Mo vs. Al-2Si	49.5	-10.4	-29.5
U-12Mo vs. Al-5Si	18.5	-3.34	-9.5

* Analysis in Progress

Interdiffusion Zone Developed Thickness

600°C for 24 Hours

Diffusion Couple	Average Thickness (µm)
U-7Mo vs. 6061Al	658
U-7Mo vs. Al	275
U-10Mo vs. 6061Al	1550
U-10Mo vs. Al	405
U-12Mo vs. 6061Al	925
U-12Mo vs. Al	223

550°C for 24 Hours

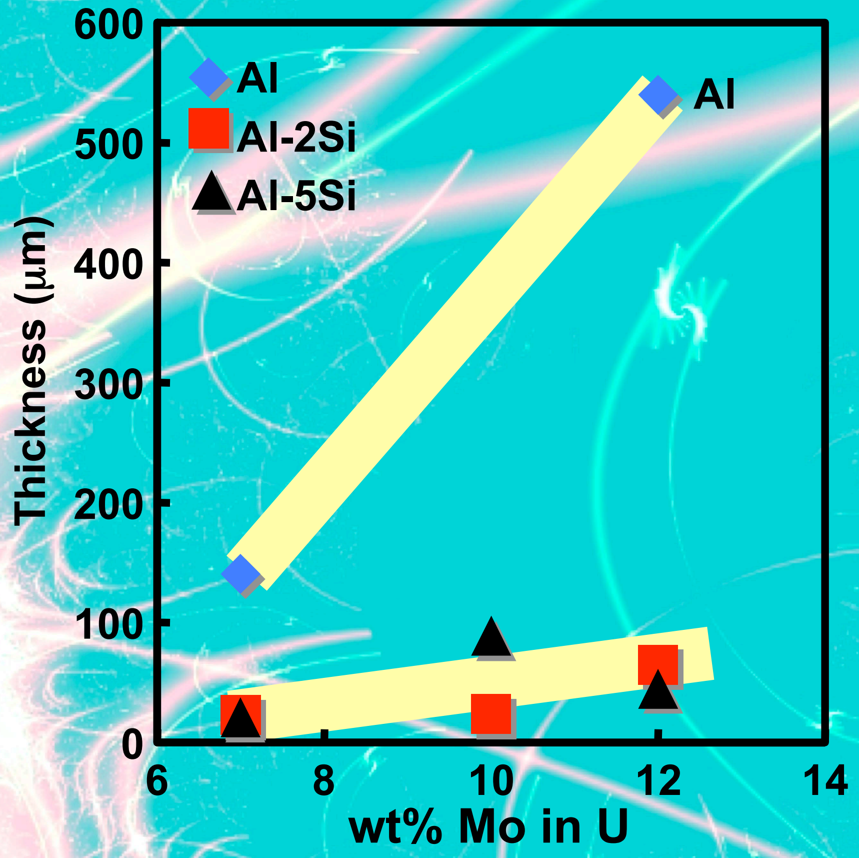
Diffusion Couple	Average Thickness (µm)
U-7Mo vs. 4043Al	24
U-7Mo vs. 6061Al	741
U-7Mo vs. Al	*
U-7Mo vs. Al-2Si	24
U-7Mo vs. Al-5Si	22
U-10Mo vs. 4043Al	*
U-10Mo vs. 6061Al	400
U-10Mo vs. Al	*
U-10Mo vs. Al-2Si	24
U-10Mo vs. Al-5Si	89
U-12Mo vs. 4043Al	28
U-12Mo vs. 6061Al	467
U-12Mo vs. Al	540
U-12Mo vs. Al-2Si	65
U-12Mo vs. Al-5Si	45

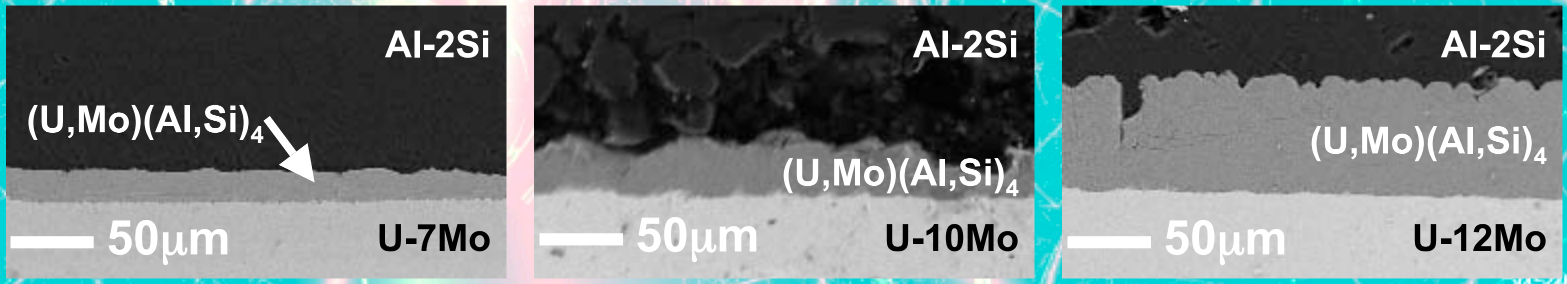
* Analysis in Progress

- **Diffusion couples with 6061 developed large interdiffusion zones.**
- **Diffusion couples with Si containing Alloys developed interdiffusion zones roughly one order of magnitude smaller than those with 6061.**

Composition Dependent Growth Kinetics of UAl_4 Intermetallic Phase at 550ºC

- The thickness of intermetallic layer increases with increasing concentration of Mo in the UMo alloy.





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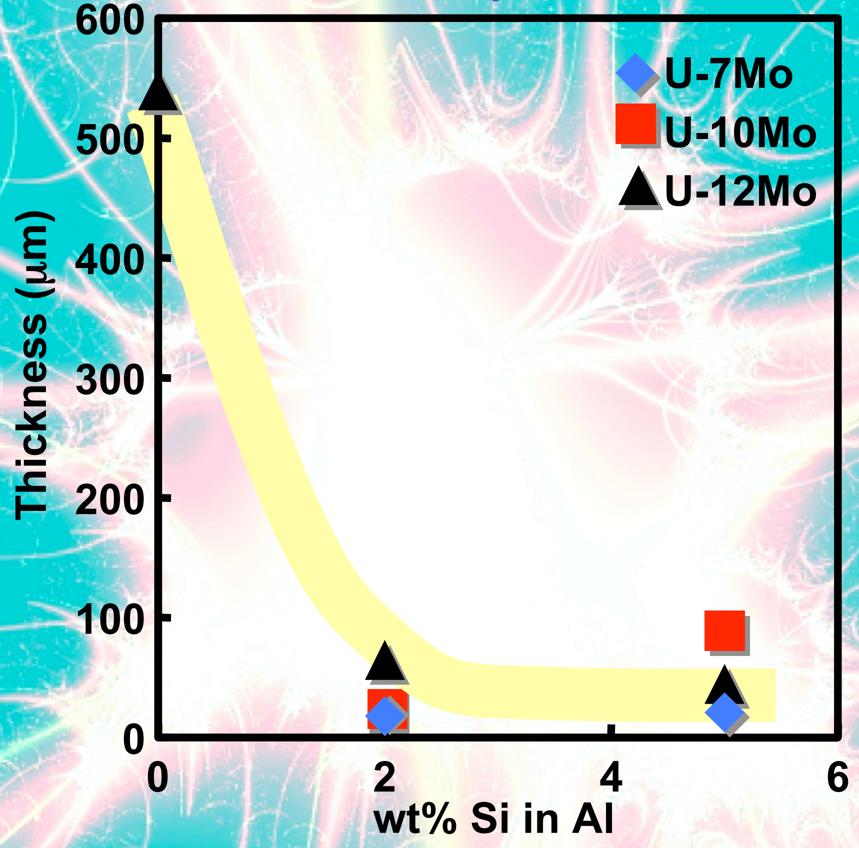
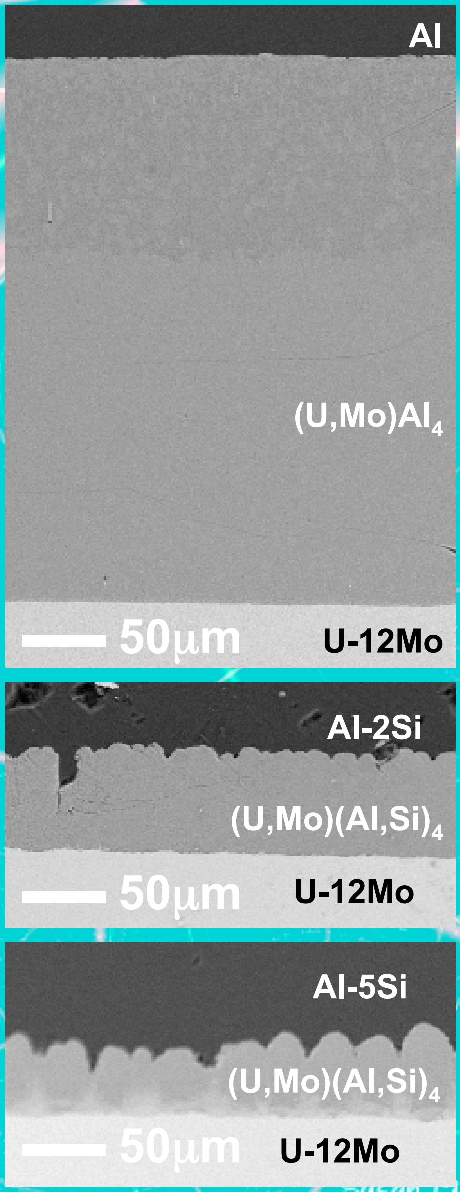
Composition Dependent Growth Kinetics of UAl_4 Intermetallic Phase at 550ºC



- The thickness of intermetallic layer in the couples with Al-Si alloys is an order of magnitude smaller than that with pure Al.
- The behavior of 4043 alloy is similar to that of Al-Si (2 and 5 wt.% Si) alloys.



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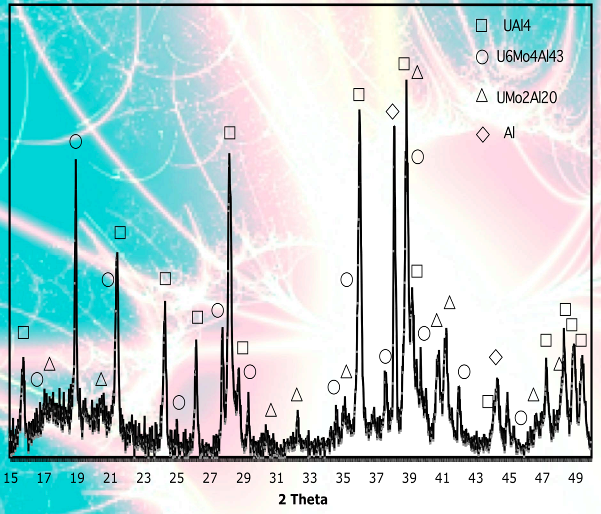
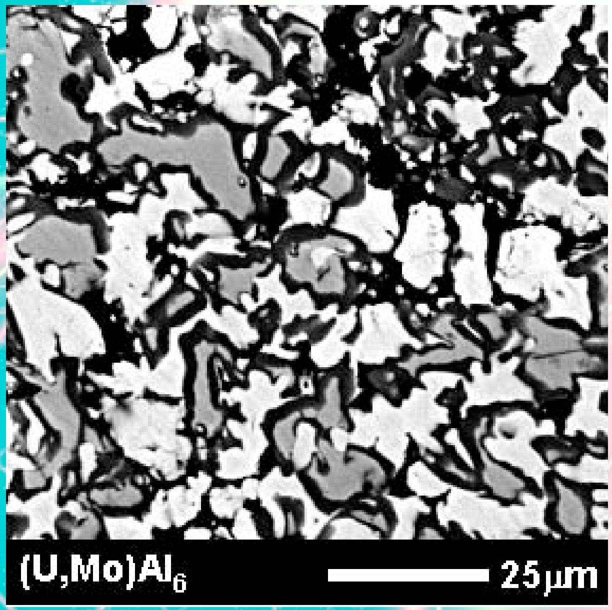
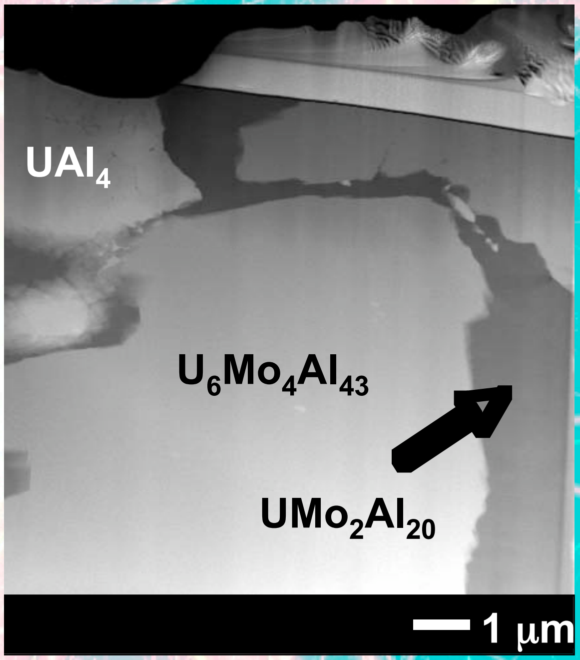
Phase Identification of Al-Rich Intermetallic Phases in U-Mo-Al System

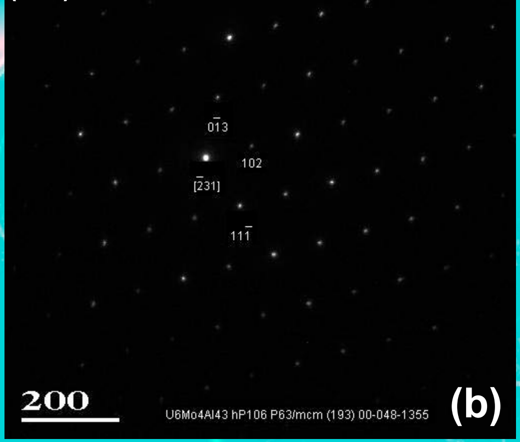




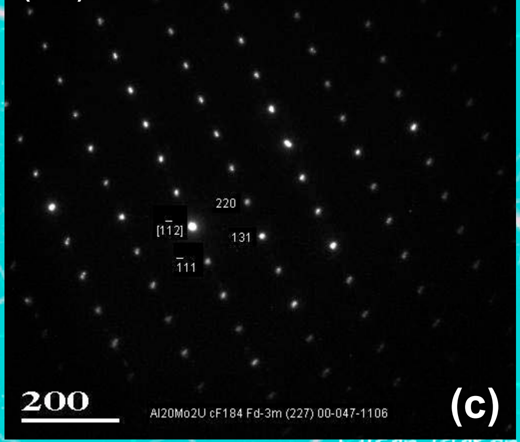


Hexagonal $U_6Mo_4Al_{43}$
Cubic UMo_2Al_{20}

Hexagonal $U_6Mo_4Al_{43}$ hP106 P63/mcm (193) 00-048-1355



Cubic UMo_2Al_{20} cF184 Fd-3m (227) 00-047-1106



Summary

- Introduction of Si into the Al Alloy in the diffusion couples appears to effectively reduce the growth rate of the intermetallic layers in diffusion couple studies.

- The composition of the intermetallic phase in all diffusion treated at 550°C and 600°C couples maintain the UAl_4 with minor solid solutioning, but with some build-up near interfaces.

- Growth rate of the UAl_4 intermetallic layer increases slightly with Mo content and decreases rapidly with Si content.

- Diffusion couples with Si in the Al-alloy exhibits a build-up of Si within the intermetallic layer in the interdiffusion zone.

Current Work in Progress

- Diffusion anneal at 500°C and 300°C.
- Determination of activation energy of interdiffusion based on integrated interdiffusion coefficients.
- Detailed phase identification within diffusion couples using TEM via FIB-INLO with particular emphasis on precipitates near interfaces.
- Other alloying additions into fuel or cladding or as coatings:
  - ✓ U-Mo-X (X = Si, Ti, Zr, Nb, etc.)
  - ✓ Diffusion barrier coatings

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