Further Insight Into Mechanisms of UMo/Al Interaction

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Outline

Overview of the French out of pile research program

Principles of the thermal ageing and diffusion couples studies

Results

- **Facts**
- **Analysis**

Concluding remarks & Perspectives

Overview of the French out of pile research program

Equilibrium Phase Diagram studies

- Experimental determination of the Equilibrium Phase Diagram
- Cristallographic studies + thermodynamic data calculations

In-pile behaviour

- Irradiation experiment (OSIRIS, BR2…)

$\Rightarrow$ PIE / modelling / simulation

Metallurgical/Diffusion studies (chemistry/mass transport/materials)

- Study of the evolution of the system far from equilibrium

Simulation of irradiation damages (heavy ion irradiation)

- Influence of the irradiation damage on the reactivity

To improve the knowledge and assess alternative solutions

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⇒ **Thermal activation of the UMo/Al interaction**

(i) Ageing of fuel plates

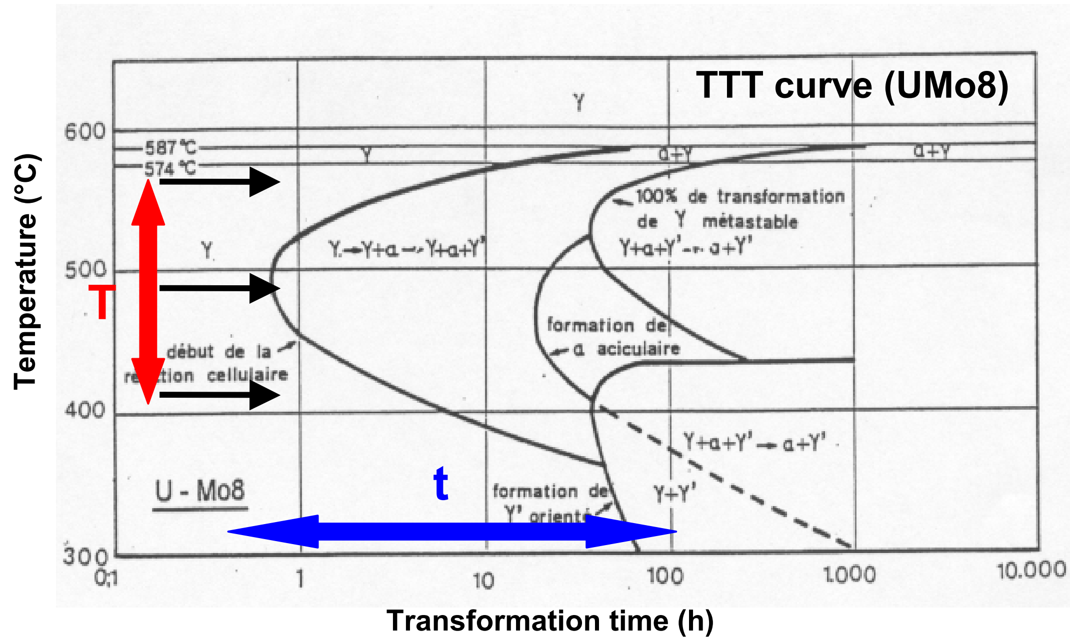
(ii) Diffusion couple studies

2 approaches

Understanding experiments ⟷ **Innovative and promising material solutions for a LEU fuel**

Principles of thermal ageing and diffusion couple studies

Parameters (T, t)



- **T > 565°C (T_E) : γ existing field**
- **T ≈ 500°C : γ ⇒ α + γ'**
- **T ≈ 400-450°C : γ metastable process T**

+ Influence of Mo on the interaction ?

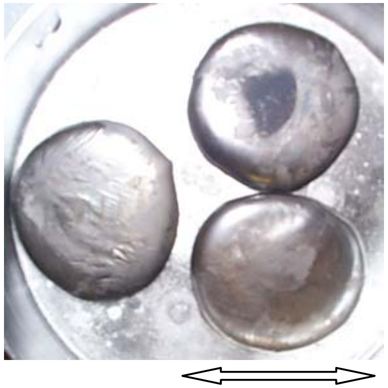
Raw materials

⇒ **UMo ingots (arc melted)** ***UMo0*, 5, 7 et 10 $\%_{wt}$ Mo**

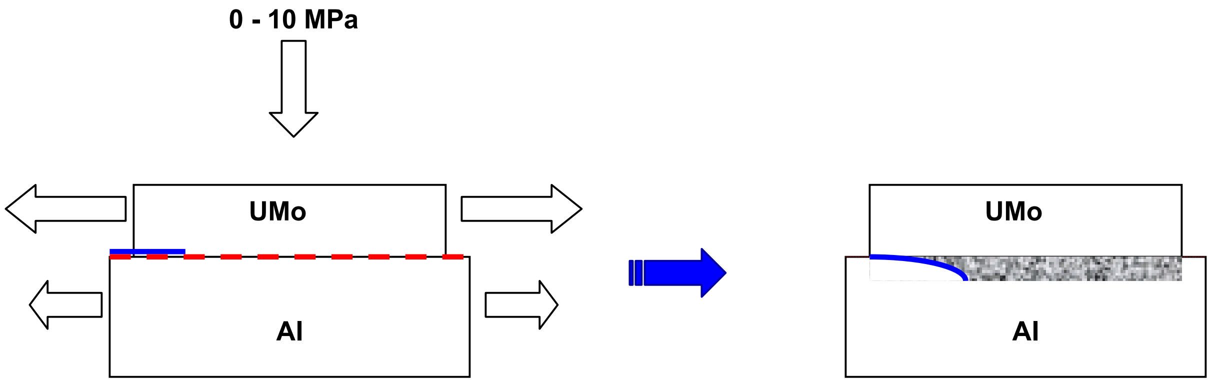
- **As-cast or**
- **Annealed (900°C / 72h) + Quenched (He, 2000°C/h)**

⇒ **Aluminium grade 1050A (A5)**

Arc melted ingots



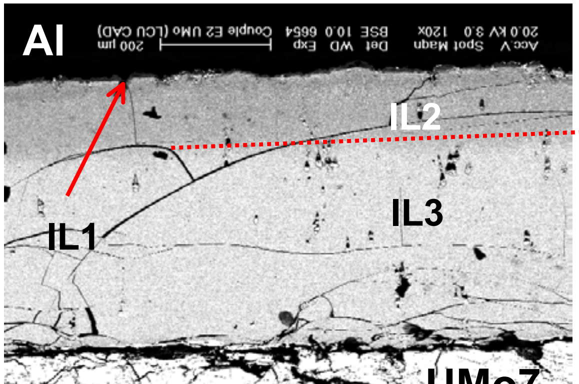
≈ 50 mm



Facts: Diffusion couple studies

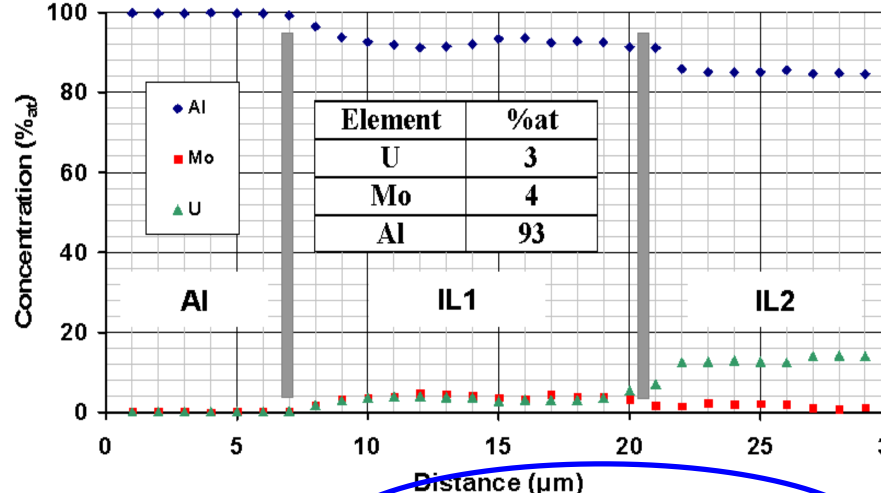
⇒ 600°C, 4h: interaction in the γ phase field

400 µm



SEM/BSE

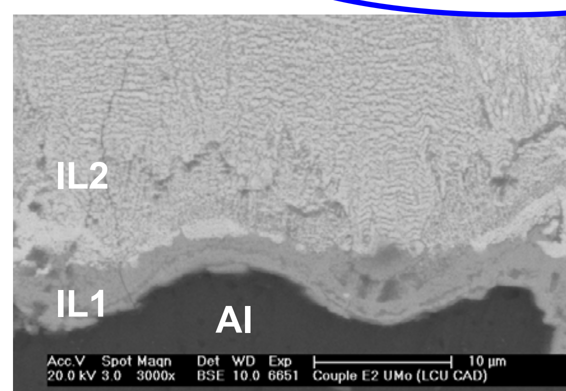
⇒ **Three-layered interaction IL1/IL2/IL3**



SEM/EDS ⇒ **Mo enrichment close to Al**

IL1 analysis (close to Al)

⇒ UMo_2Al_{20}



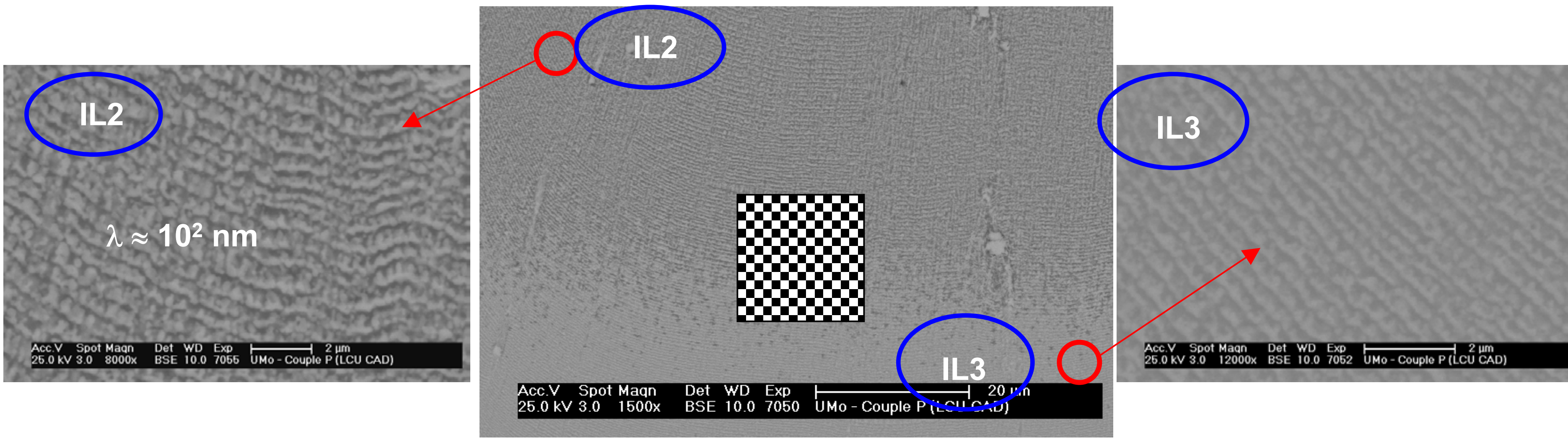
10 µm

Consistent with *Ryu et al., J. Nucl. Mater. 321 (2003) 210, and Mirandou et al., J. Nucl. Mater. 323 (2003) 29*

Facts: Diffusion couple studies

⇒ 550°C, 1h: interaction in the γ phase field

- Periodic Layers : Periodic sequence of mono or polyphased (?) layers



- IL2 and IL3 differ in composition (SEM/BSE : Z contrast observed)
- ⇒ IL2 : $UAl_4 + UMo_2Al_{20}$

  ⇒ IL3 : $UAl_3 + U_6Mo_4Al_{43}$

What are the monolayers made of ?

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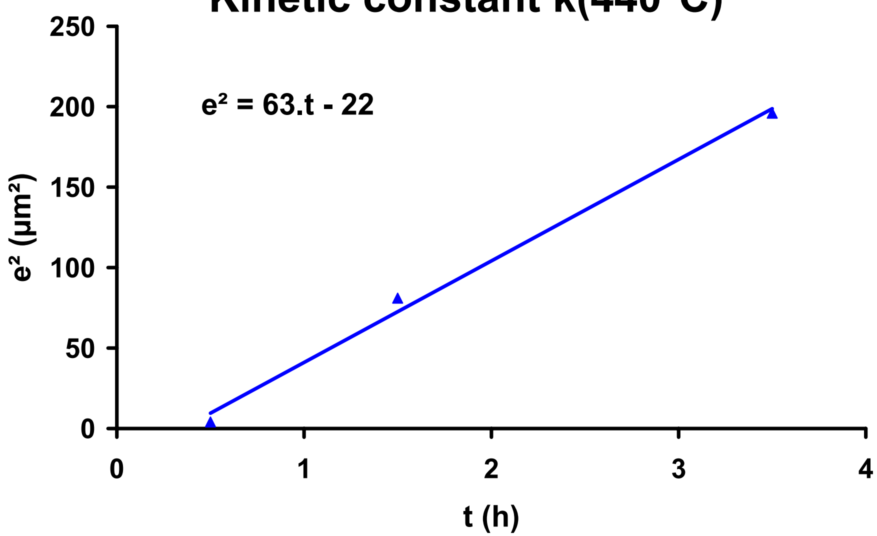
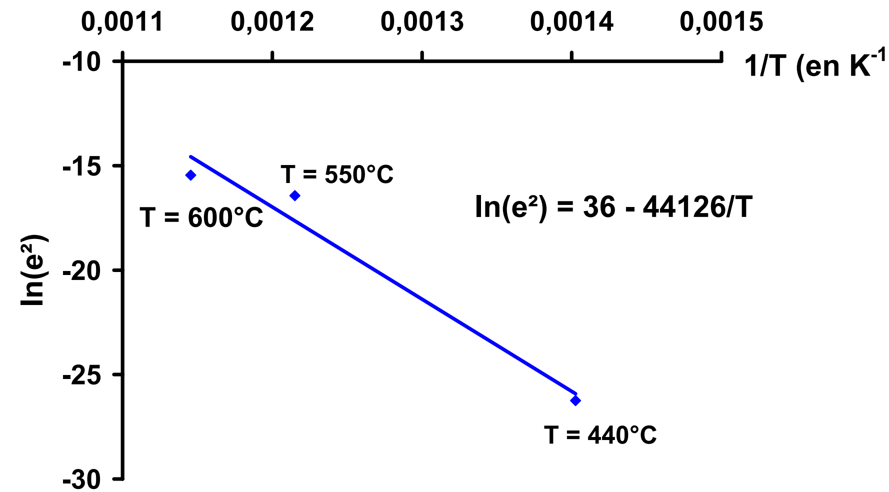
⇒ A few kinetics aspects of the γ-UMo/Al interaction

UMo10 – 440, 550, 600°C

Kinetic constant k(440°C)



Global activation energy (1h)



$$e^2 = k.t$$

$$k = k_0.\exp(-Q/RT)$$

$$\ln(e^2) = \ln(k_0.t) - Q/RT$$

⇒ k_{UMo10} (440°C) = 63 µm²/h

⇒ Q_{UMo10} (1h) = 360 kJ/mol

316 kJ/mol [Ryu et al., J. Nucl. Mater. 321 (2003) 210]

Bulk diffusion controlled growth mechanism

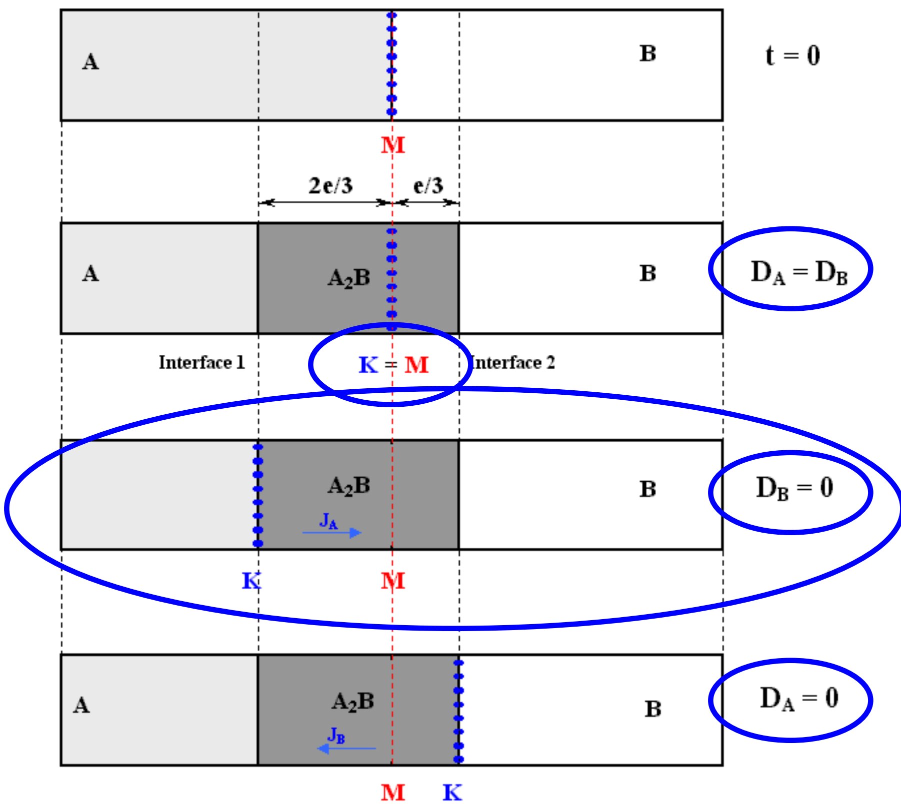
⇒ A few kinetics aspects of the γ-UMo/Al interaction

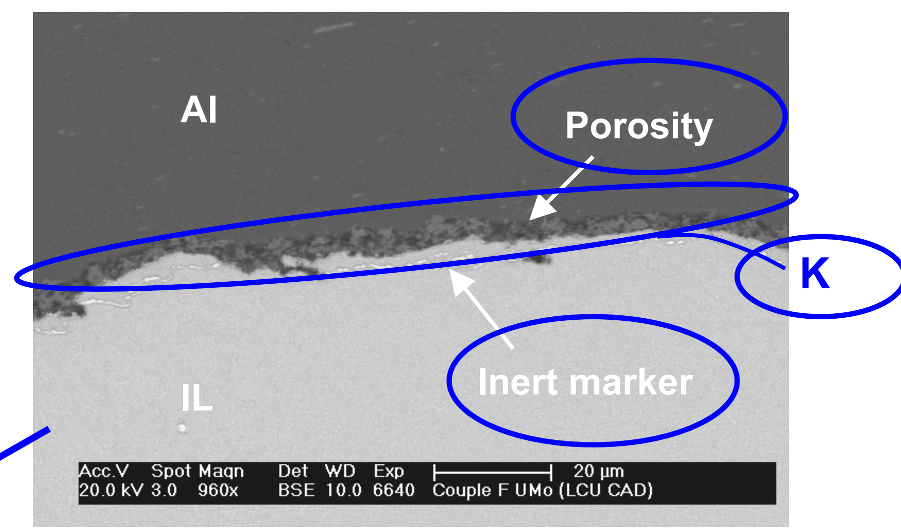
Evidence of the Kirkendall effect

Matano plane M : atom number conservation

Kirkendall plane K : site number conservation

Inert markers





UMo7/Al

Al = dominant diffusing specie

⇒ A few kinetics aspects of the γ-UMo/Al interaction

Influence of Mo

- Same phases and same morphology whatever the Mo content (if > 5%wt)
- The ratio of ternary compounds increases with the Mo content

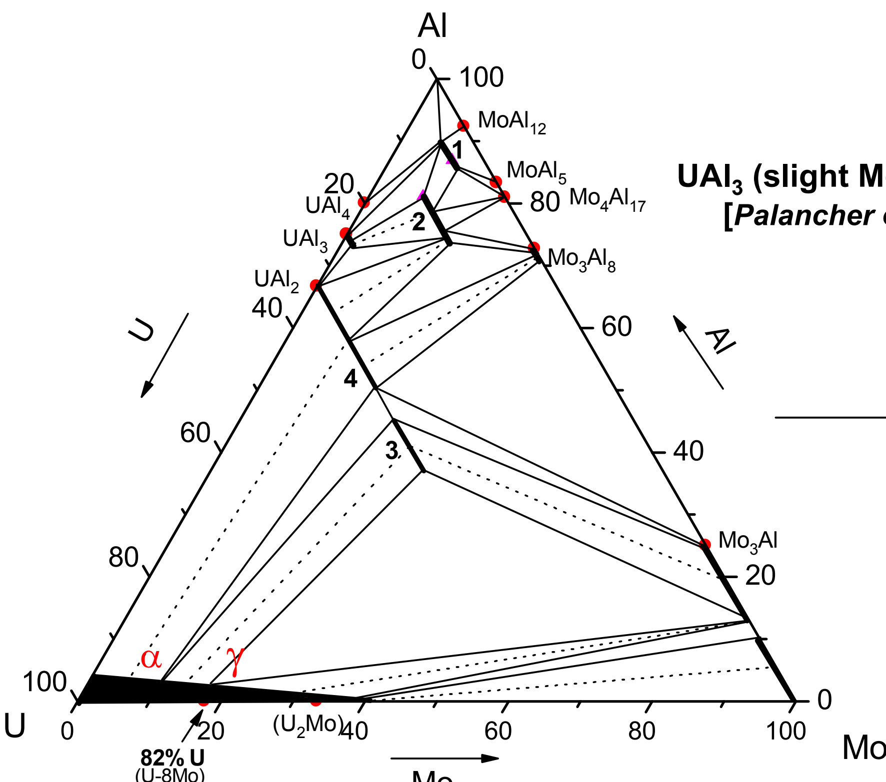
Conditions	%wt Mo	IL thickness (µm)	IL3 thickness (µm)
550°C 1h	5 et 7	> 1000	≈ 400
	10	> 500	200
425°C 1h	7	270	
	10	2	

- Dramatic decrease of the interfacial reactivity with increasing Mo-content

Al diffusion in ternary compounds = growth rate limiting step

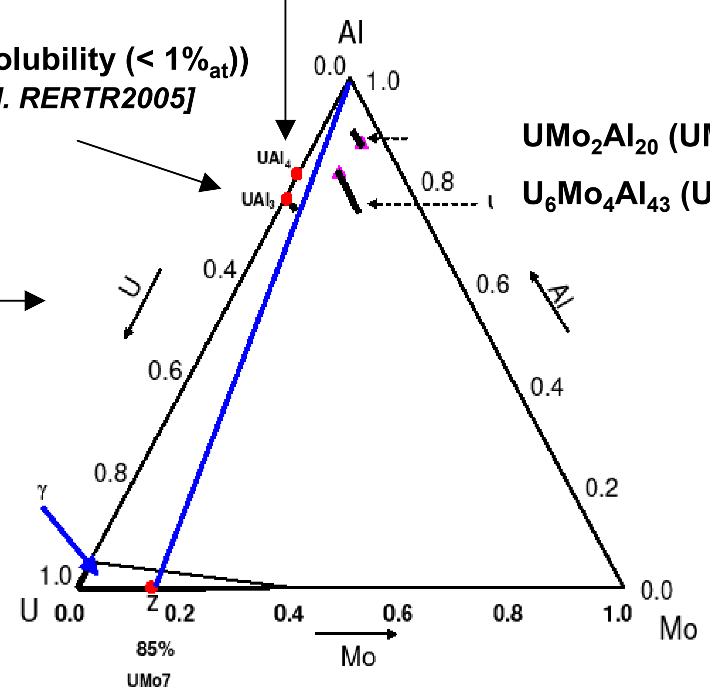
A thermodynamic approach for the formation of the periodic layers

Metastable ternary diagram U-Mo-Al with relevant (encountered) phases



UAl_3 (slight Mo solubility (< 1%$_{at}$))
[*Palancher et al. RERTR2005*]

UAl_4 (binary, stoichiometric)
[*Tougait, Intermetallics 12 (2004) 219*]



UMo_2Al_{20} ($UMo_{2\pm x}Al_{20\pm x}$)

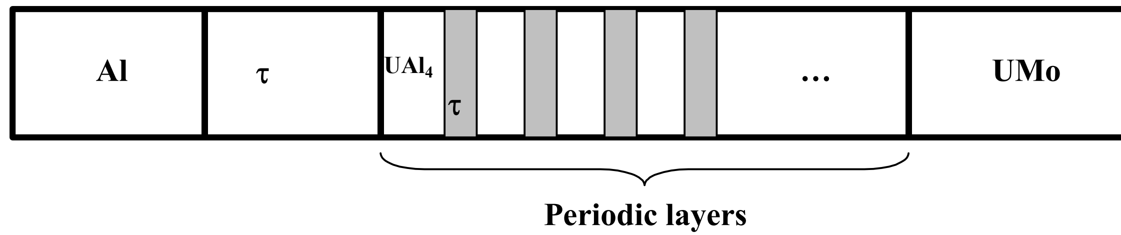
$U_6Mo_4Al_{43}$ ($U_6Mo_{4+x}Al_{43-x}$)

Mass balance boundary line ≠ Diffusion path

Analysis

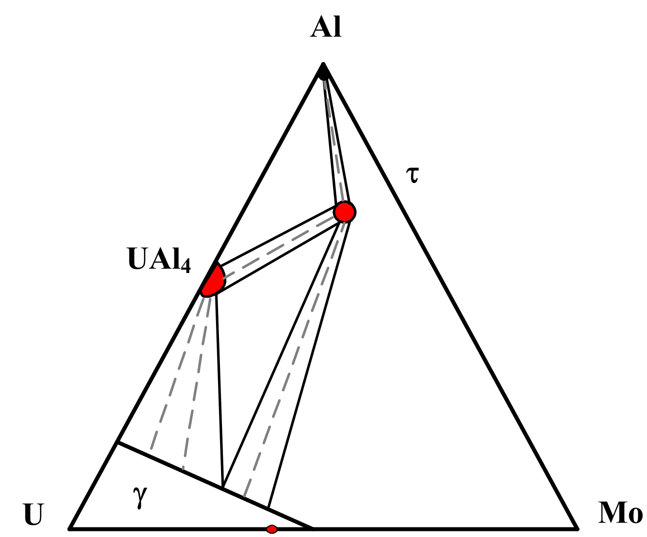
A thermodynamic approach for the formation of the periodic layers

Simplified Configuration (morphology)



D_{Al} (Zl) >> $D_{U,Mo}$ (Zl)

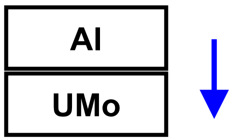
Driving force : grad(μ_{Al}) < 0



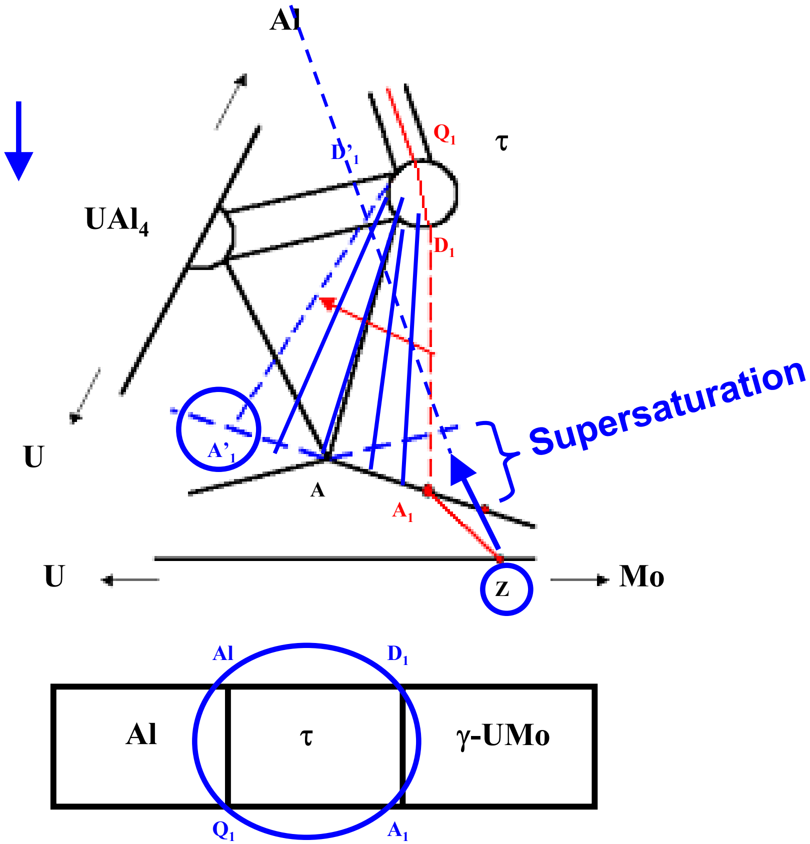
Assumptions : single phase layer

A VERY simplified representation…

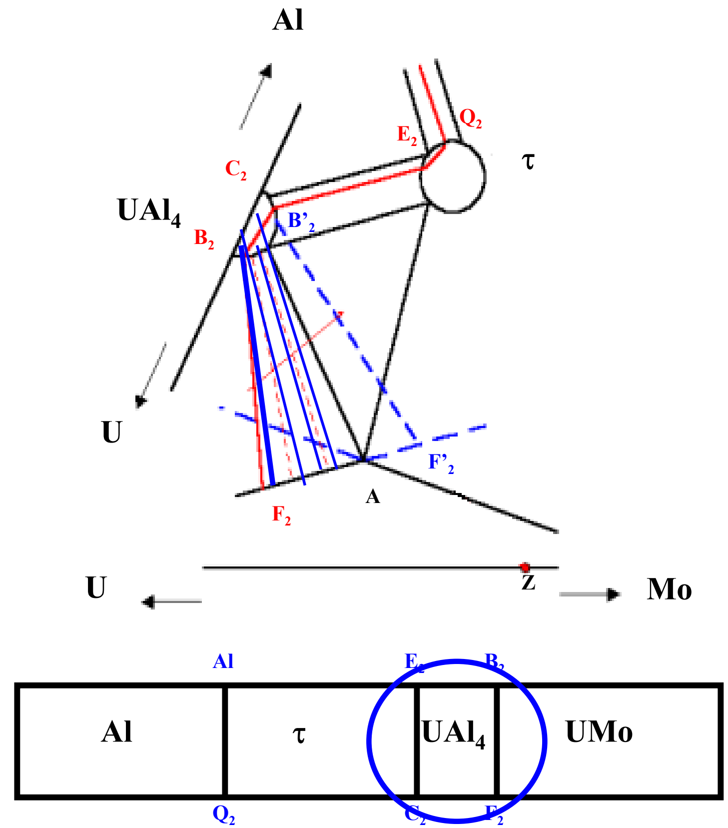
A thermodynamic approach for the formation of the periodic layers



Growth of τ layer (IL1)



Growth of UAl_4

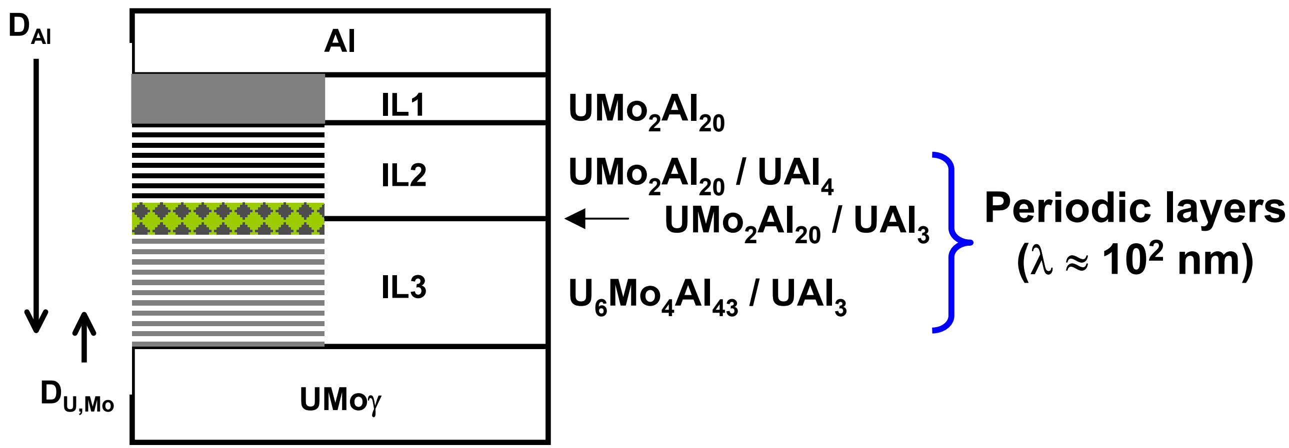


Repetition of the phenomenon = formation of the periodic layer

Concluding remarks : Advances in understanding UMo/Al interaction

550°C < T < 600°C

- **1 : γ-UMo + Al $\Rightarrow$ UAl_4 + UAl_3 + UMo_2Al_{20} + $U_6Mo_4Al_{43}$**
- **2 : Three-layered morphology :**
  IL1 = UMo_2Al_{20}
  IL2 = UAl_4 + UMo_2Al_{20}
  IL3 = UAl_3 + $U_6Mo_4Al_{43}$
- **3 : Global growth kinetic limiting step = Al bulk diffusion in ternary compounds**
- **4**



- ***T ≈ 500°C :*** **γ-UMo $\Rightarrow$ γ'+α / Al + α $\rightarrow$ UAl_3 and Al + γ' $\rightarrow$ $U_6Mo_4Al_{43}$**
- ***T < 450°C : n-layered morphology (work in progress….)***

Perspectives

- **Refining the data and integration of results on the UMo/Al reference system**

- **Assessment of new UMo LEU fuel concepts using a similar approach, e.g.**
  - **Alloying Al matrix with a tetravalent (+IV) element**
  - **Alloying U with other gammagen metal**