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# As-fabricated Nitride and Silicide Coated U-Mo Atomized Particles Complementary Microstructural Analyses

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DE LA RECHERCHE À L'INDUSTRIE



# AS-FABRICATED NITRIDE AND SILICIDE COATED U-MO ATOMIZED PARTICLES: COMPLEMENTARY MICROSTRUCTURAL ANALYSES

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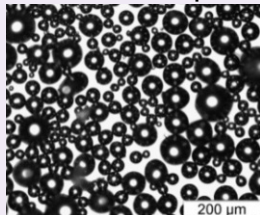
# U-MO/AL SAMPLE MANUFACTURING (NO-CLADDING)



## U-Mo Powder

### Atomization

$90 < \varnothing < 150 \mu\text{m}$



## Coating

Solid/gas reaction  
Solid/solid reaction



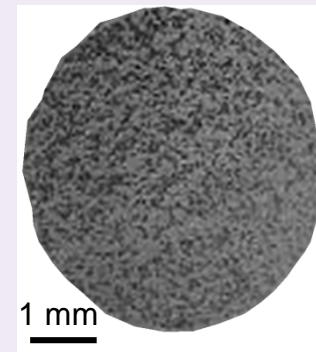
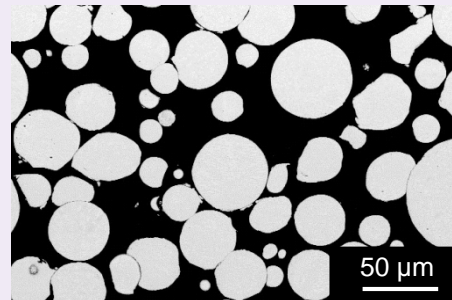
## U-Mo/Al Compact

Powder blending  
Compaction

**Extrusion**  
 $T < 450^\circ\text{C}$   
Duration  $\approx 1\text{h}$

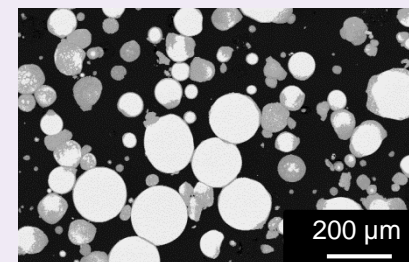
## As-fabricated fuel meat

### Upper view



## Post-manufacturing annealing

Temperature:  $580^\circ\text{C}$   
Duration: 1h



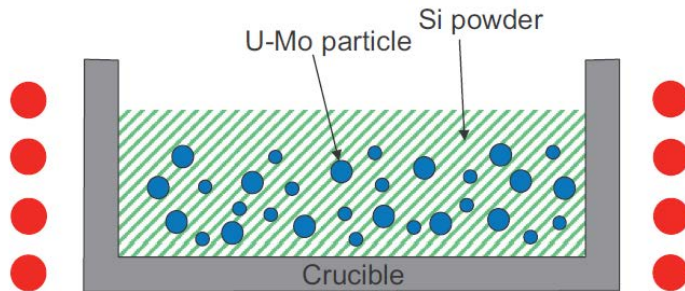
W.J. Kim *et al.*, J. of Alloys and Comps 589 (2014) 94–100.

# COATING CONDITIONS FOR THE U-MO POWDER (KOMO-5 TEST)

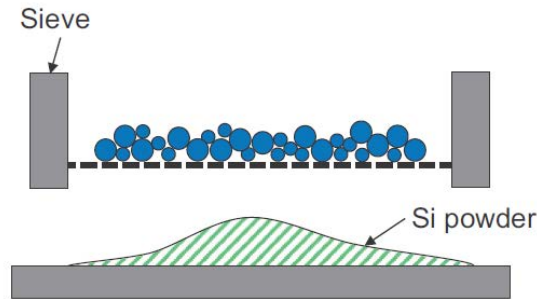
H.J. Ryu et al., Nucl. Eng. Technol. 43 (2011) 159-166.

Y.S. Kim et al., J. Nucl. Mater. 454 (2014) 238-246

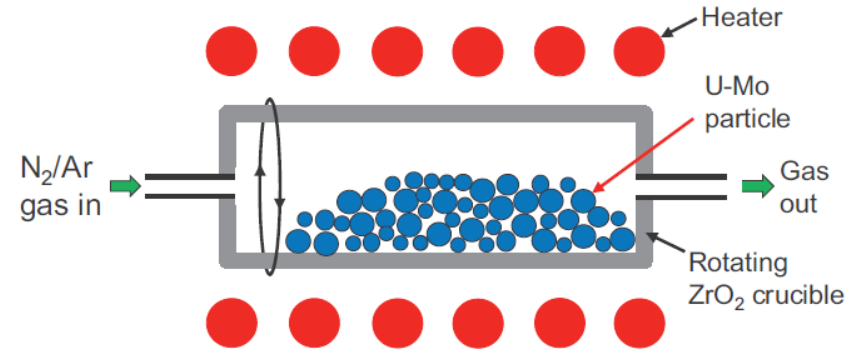
## Si coating



Vacuum heating at 1000 °C for 1 hour



## Nitride coating



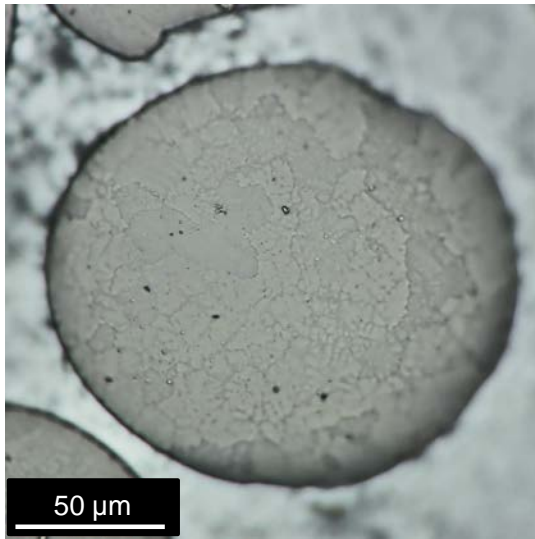
The operation conditions of nitride coating.

Parameters	Conditions
Back ground pressure	$1 \times 10^{-6}$ torr
Working pressure	$3 \times 10^{-5}$ torr
N <sub>2</sub> -gas flow	80 sccm
Revolution speed	30 rpm
Temperature	1000 °C
<i>Holding time</i>	
U-7 wt%Mo	6 h
U-7 wt%Mo-1 wt%Ti	1-4 h

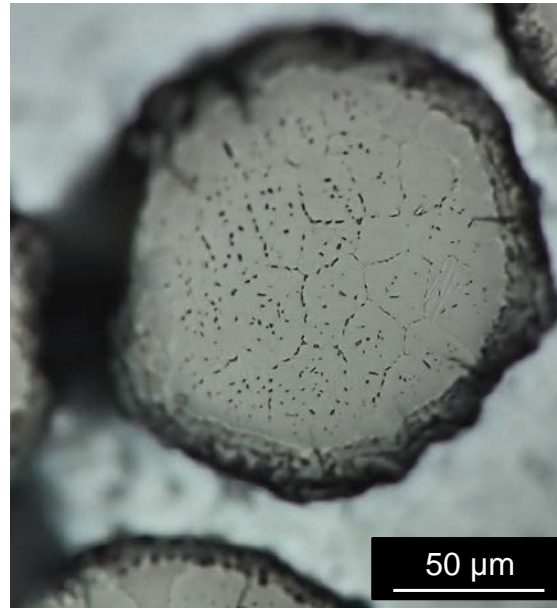
Goals of the characterisation: coating composition but also U-Mo grain size modification

# GRAIN SIZE EVALUATION USING OPTICAL MICROSCOPY

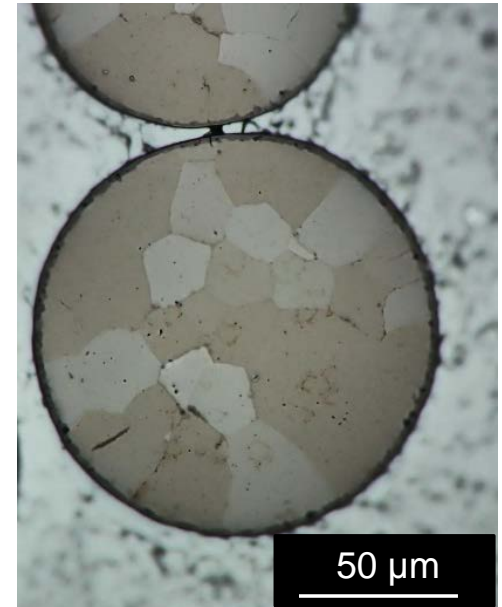
As-atomised



U-Mo(Si)  
(1000°C 1h)



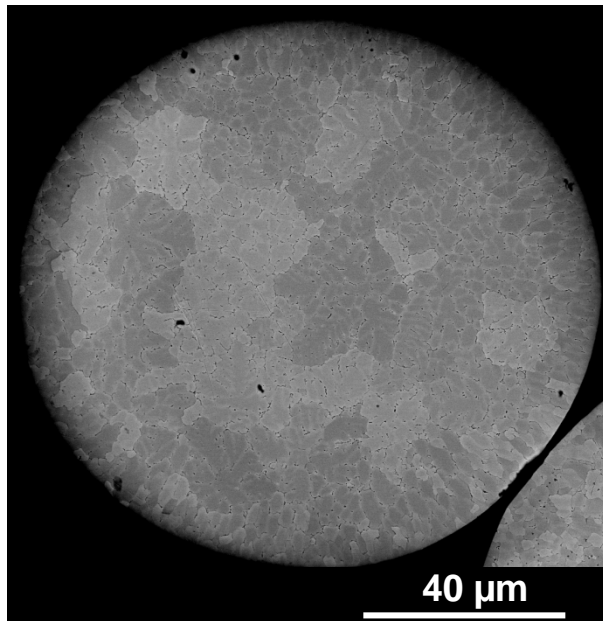
U-Mo(N)  
(1000°C 6h)



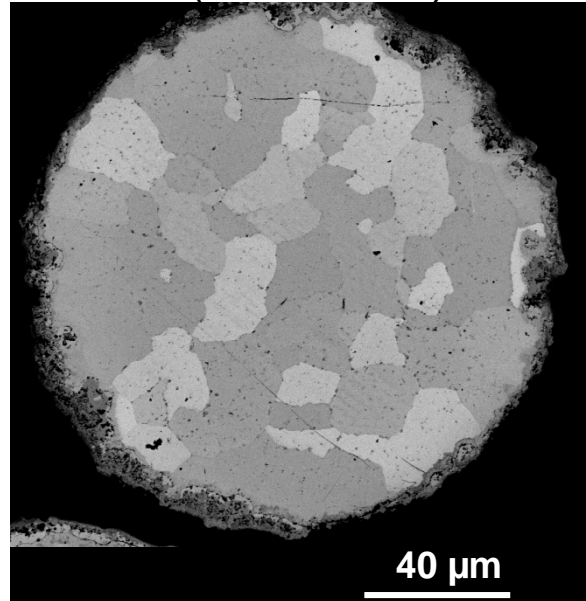


# GRAIN SIZE EVALUATION USING SEM

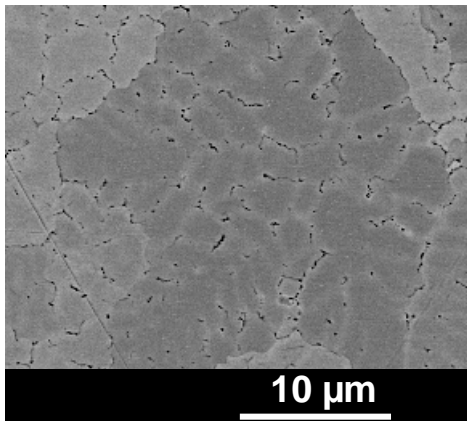
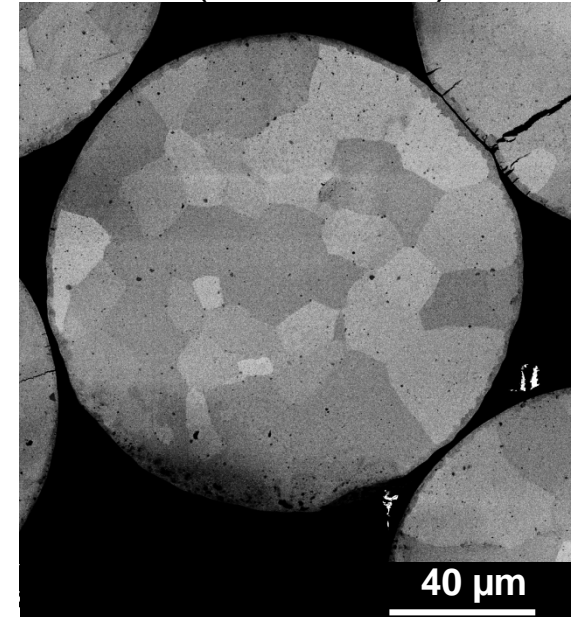
As-atomised



U-Mo(Si)  
(1000°C 1h)

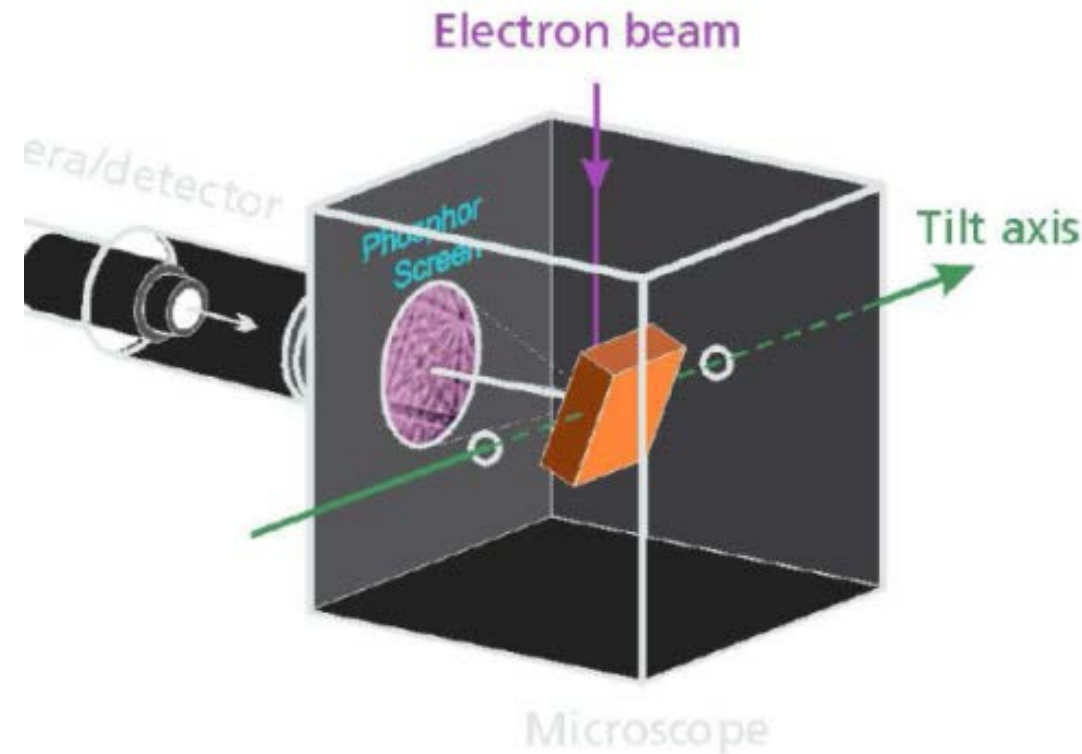
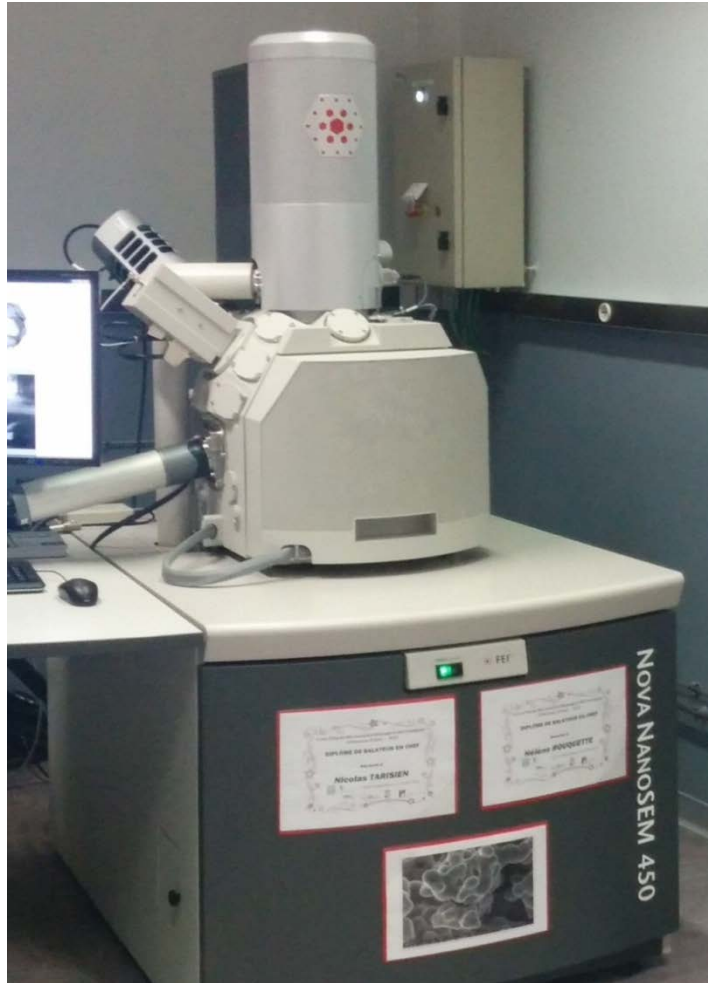


U-Mo(N)  
(1000°C 6h)



Even with high quality SEM characterisation combined with image analysis, grain size is difficult to determine accurately.

# ELECTRON BACK-SCATTER DIFFRACTION (EBSD)



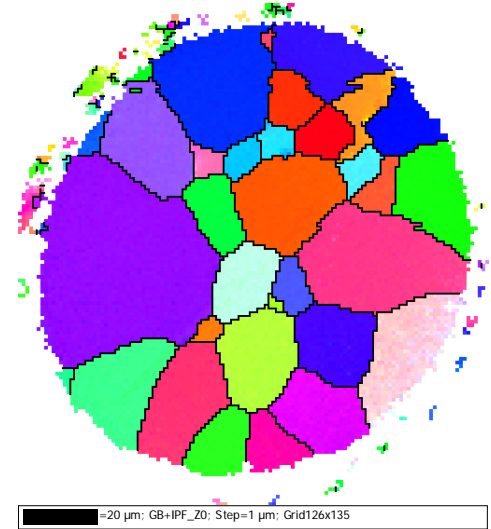
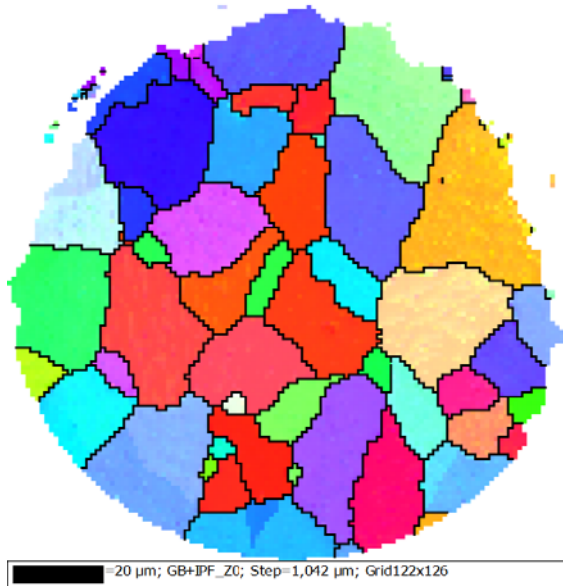
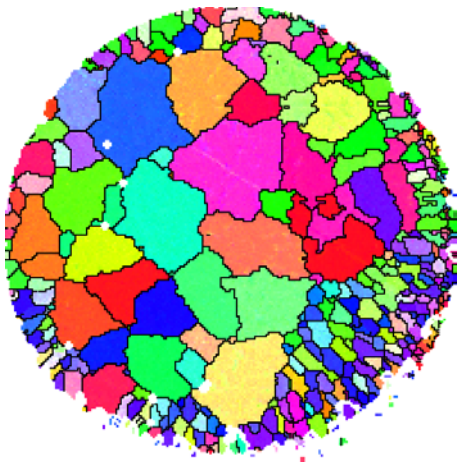
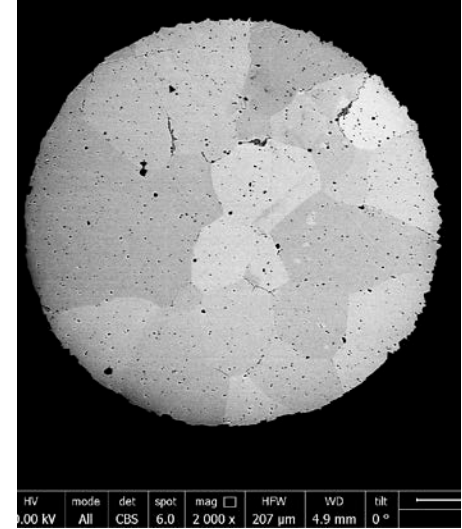
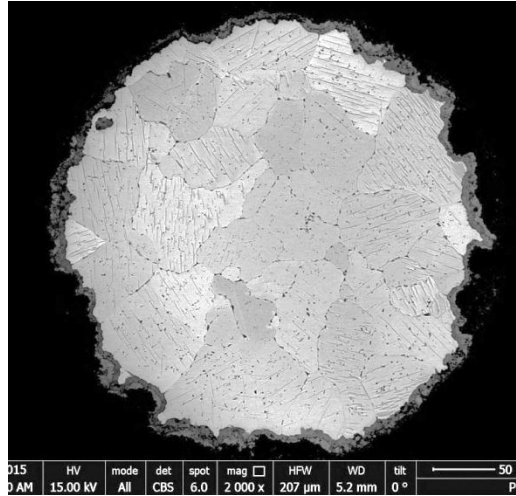
For further technical details on the application of this technique on as-atomised UMo nuclear fuel:  
See: **G. Champion, Ph.D. Thesis (Rennes University) 2013 (France).**

# GRAIN SIZE EVALUATION USING EBSD (I/II)

As-atomised

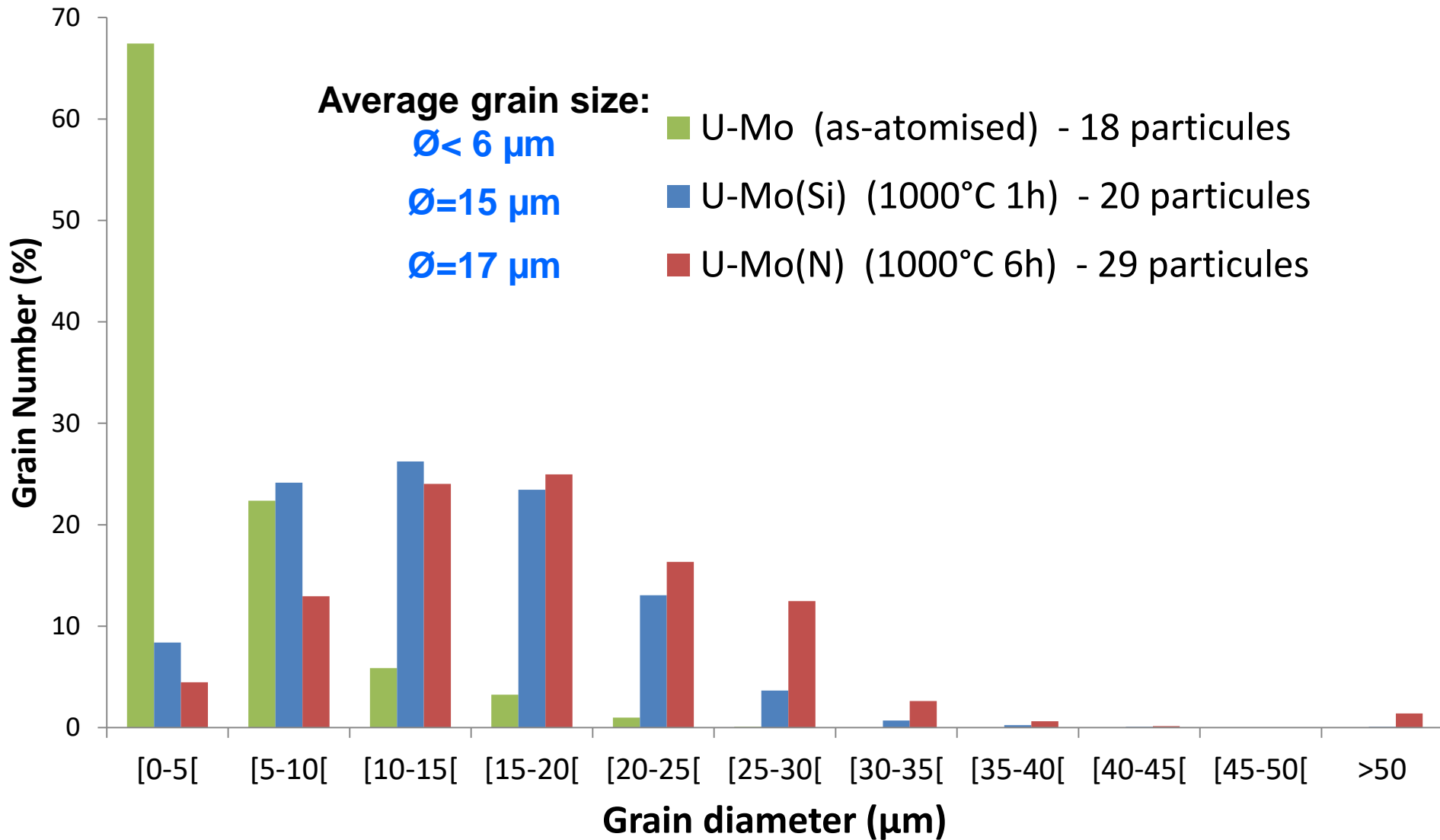
U-Mo(Si) (1000°C 1h)

U-Mo(N) (1000°C 6h)



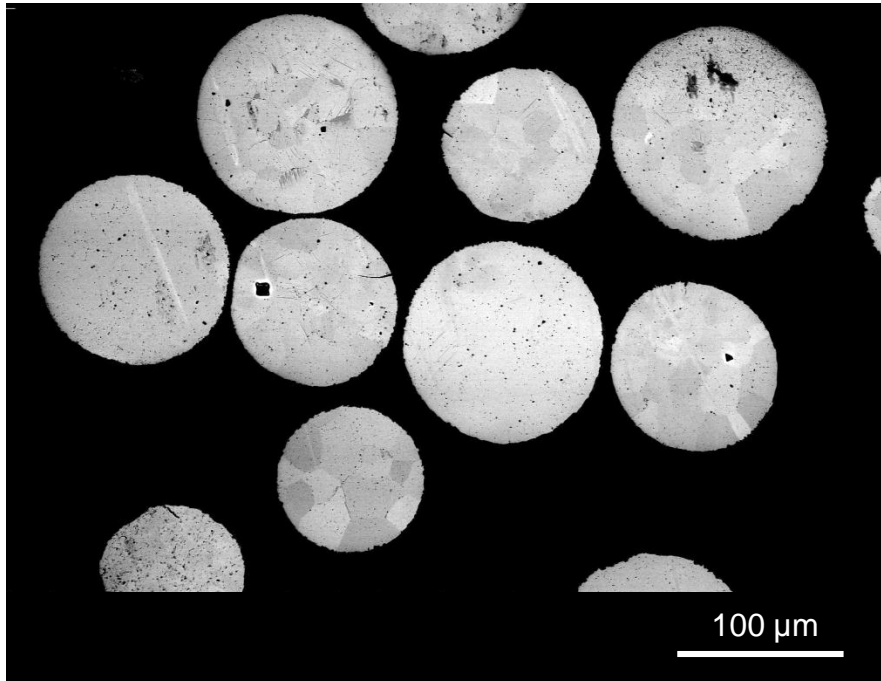


# GRAIN SIZE EVALUATION USING EBSD (II/II)

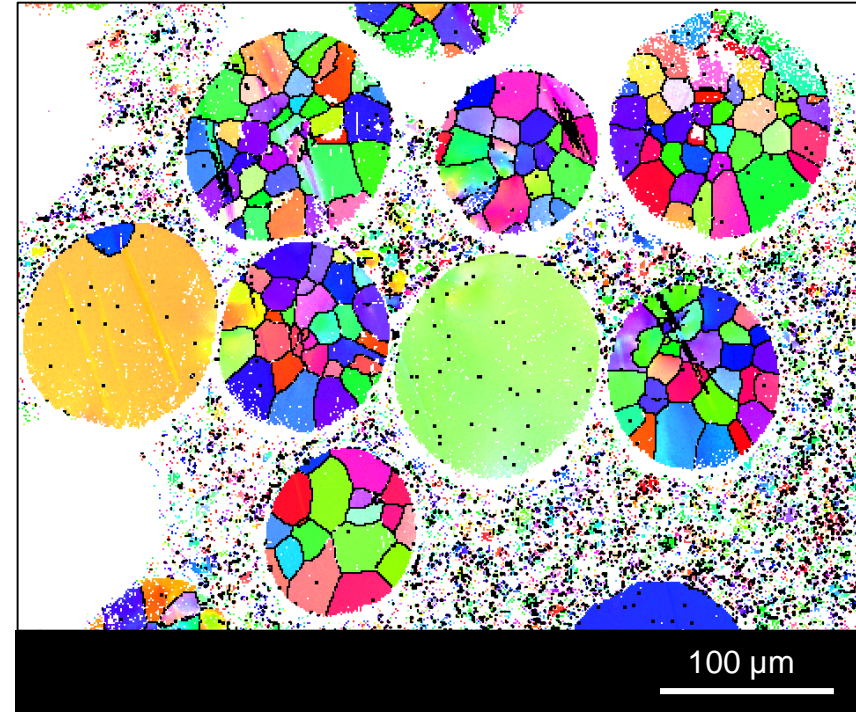


# U-MO MICROSTRUCTURE AFTER TT AT 1000°C DURING 6H: LARGE EBSD MAPS

SEM



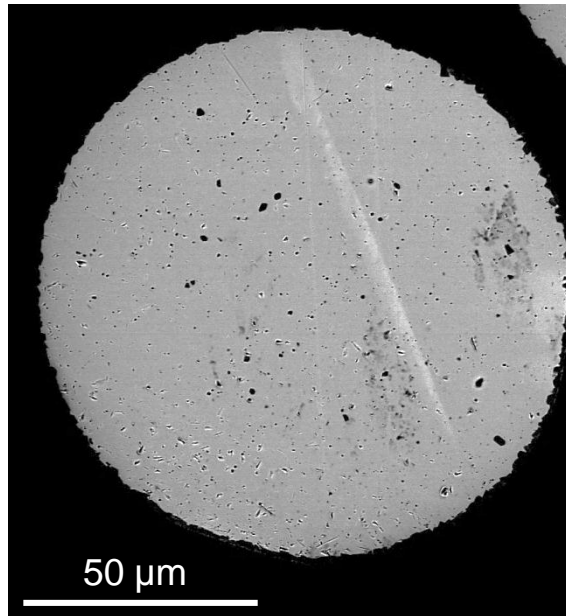
EBSD



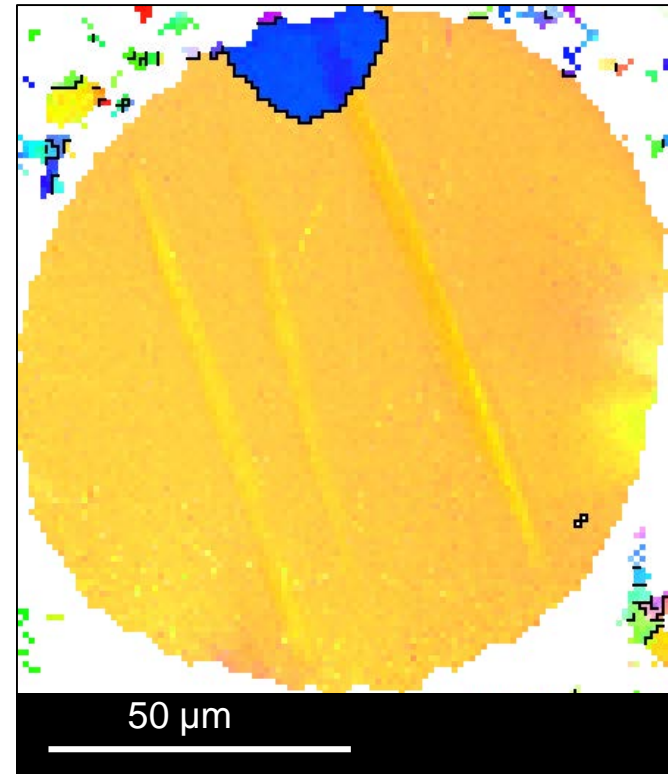
Evidence for the presence of « single crystal » U-Mo particles

# MICROSTRUCTURE AFTER TT AT 1000°C DURING 6H: SINGLE CRYSTAL PARTICLES

SEM

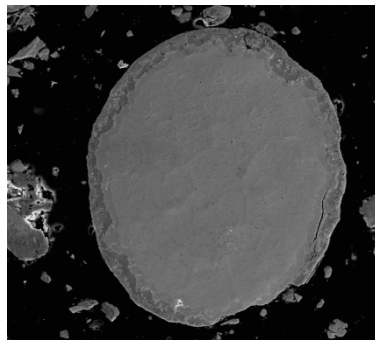
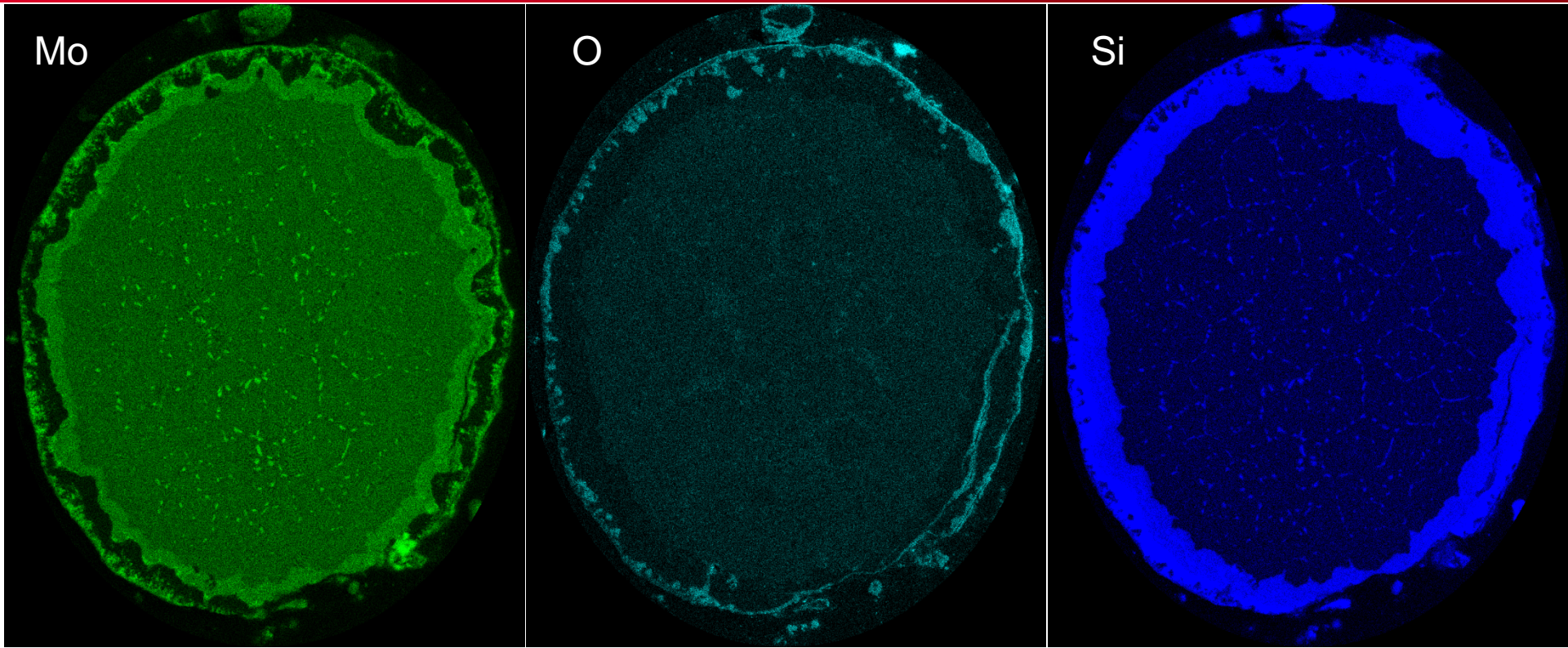


EBSD



Evidence for the presence of « single crystal » U-Mo particles

# PRECIPITATION AS A RESULT OF THE POWDER ANNEALING

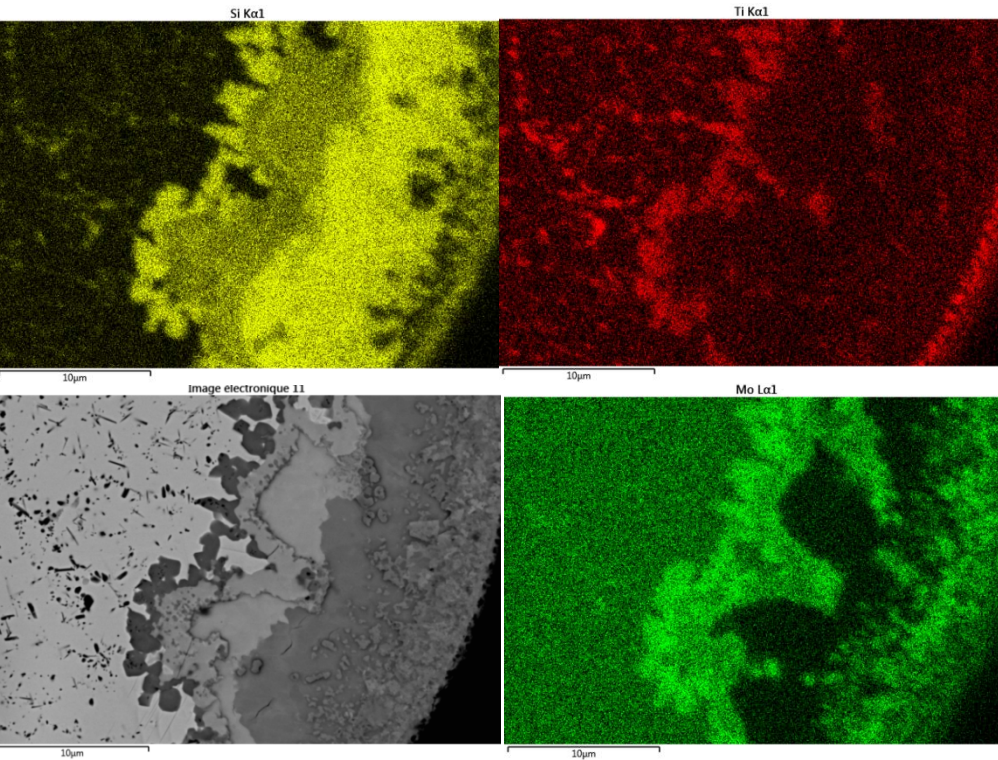


In U-Mo (Si) particles, intergranular Mo-Si rich precipitates can be observed

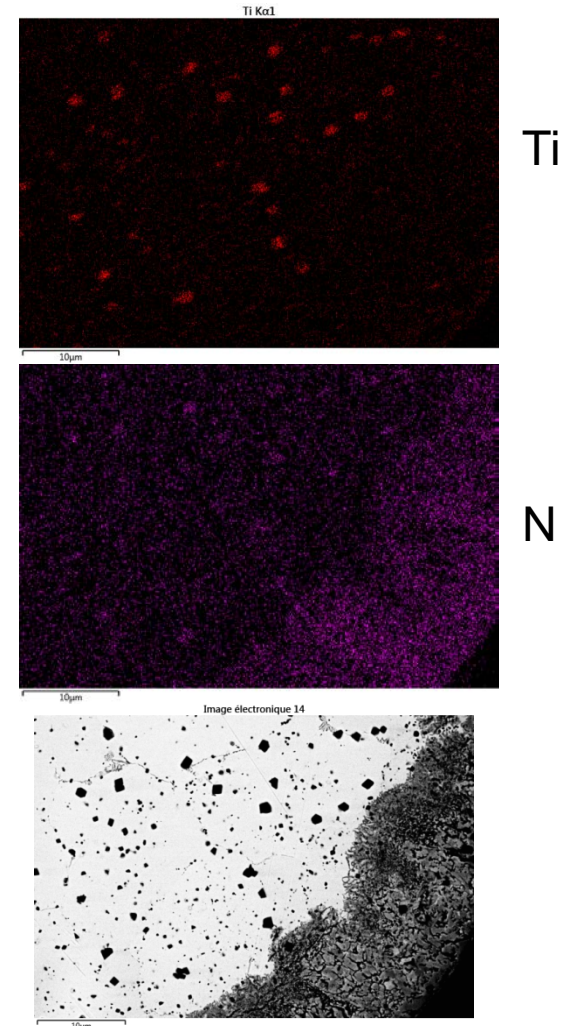


# ADDITION ELEMENTS PRECIPITATION: THE CASE OF U-MO-TI PARTICLES

U-Mo-Ti(Si)  
(1000°C 1h)



U-Mo-Ti (N)  
(1000°C 6h)



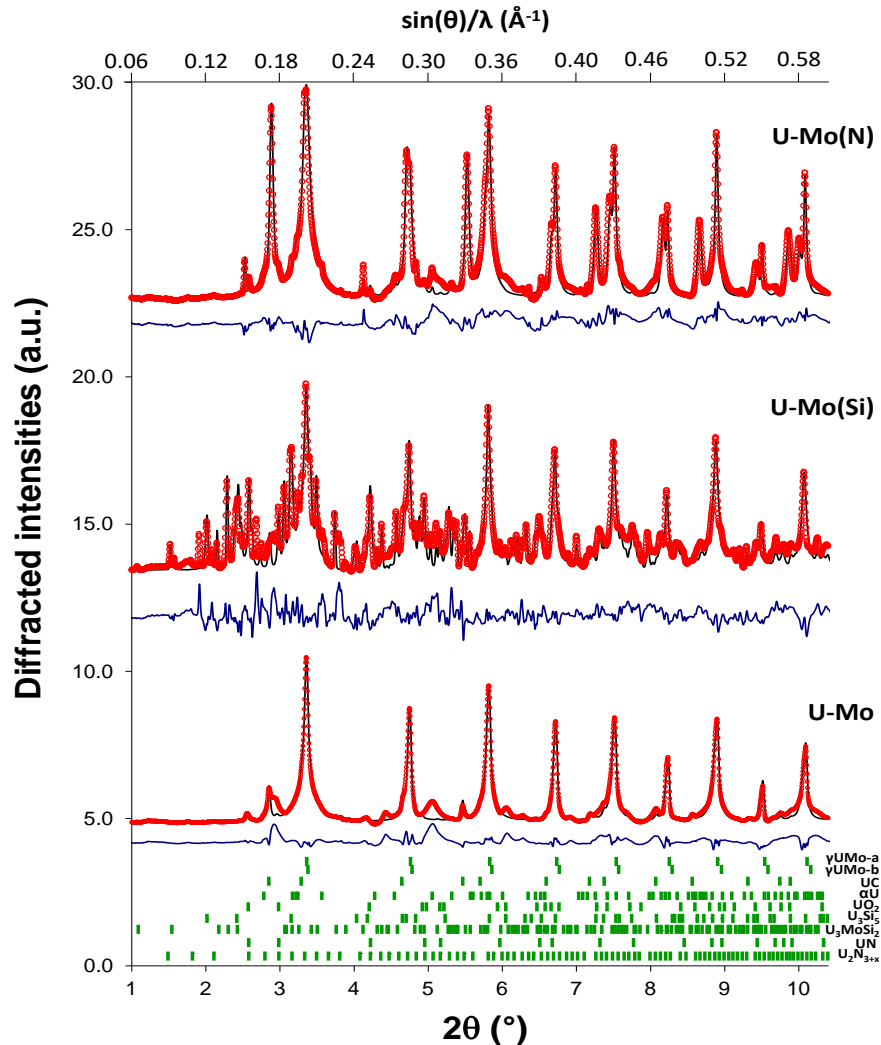
Precipitation of Ti after thermal treatments :

- into Ti, Si and probably Mo rich precipitates in U-Mo-Ti(Si)
- into TiN in U-Mo-Ti(N)



# X-RAY DIFFRACTION AT HIGH ENERGY (87 KEV)

○ Ln (Yobs) — Ln(Ycalc) — Ln(Yobs)-Ln(Ycalc)



ID15B@ESRF



- Two  $\gamma$ U-Mo lattice constants in the as-atomised case only
- Additional tetragonal superlattice
- Quantification of impurities:  
U(C,O)  
UO<sub>2</sub>

# X-RAY DIFFRACTION AT HIGH ENERGY (87 KEV)

	Weight fraction (%)									
	U-Mo core			Pollution	N Coating		Si coating			
	$\gamma$ -UMo	$\alpha$ -U	UC	UO <sub>2</sub>	UN	U <sub>4</sub> N <sub>7</sub>	USi <sub>1.88</sub>	U <sub>3</sub> Si <sub>2</sub>	U <sub>3</sub> Si <sub>5</sub>	U <sub>3</sub> MoSi <sub>2</sub>
Powder UMo	98.11	0	1.6	0.29	0	0	0	0	0	0
powder UMo(Si)	51.62	0	0	7.11	1.3	0	5.05	2.95	15.48	16.49
powder UMo(N)	59.94	1.72	0	0.91	37.4	0.02	0	0	0	0

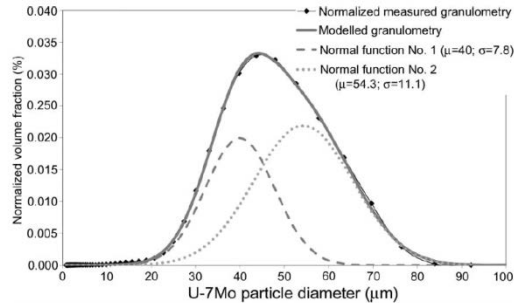
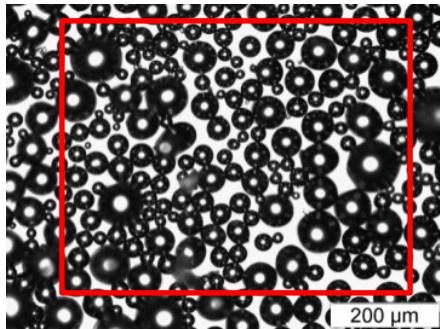
## Conclusion :

- No destabilization of the  $\gamma$ U-Mo phase (cooling rate high enough)
- Very high concentration of UN phase in U-Mo(N) (not consistent with 2-3  $\mu$ m thick coating)
- Very complex crystallographic composition of the UMo(Si) coating

	U-Mo As-atomised	U-Mo(Si) (1000°C 1h)	U-Mo(N)/Al
Destabilisation ratio	0	<5%	<5%

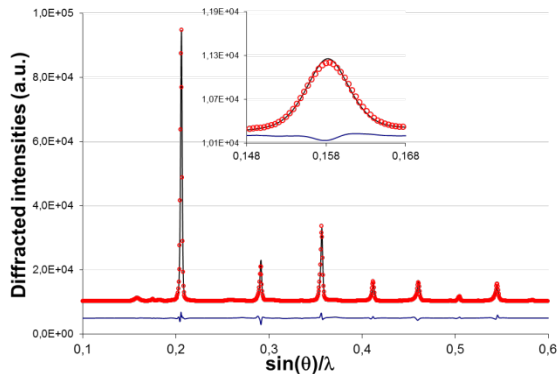
# MEASUREMENTS OF THE AVERAGE COATING THICKNESS AT A MACROSCOPIC SCALE

## HE-XRD measurements on powder sample



$$\frac{V_{\text{Shell}}^{\text{Powder}}}{V_{\text{Core}}^{\text{Powder}} + V_{\text{Shell}}^{\text{Powder}}} = \frac{\int_0^{\infty} f_V(D) V_{\text{Shell}}^{\text{Particle}} dD}{\int_0^{\infty} f_V(D) V_{\text{Shell}}^{\text{Particle}} dD + \int_0^{\infty} f_V(D) V_{\text{Core}}^{\text{Particle}} dD}$$

$$e = 0.0004V_{\text{ratio}}^2 + 0.0902V_{\text{ratio}} + 0.0013$$



## Validation of the method

Method firstly validated on 1 μm thick UO<sub>2</sub> coated U-Mo particles using tomography

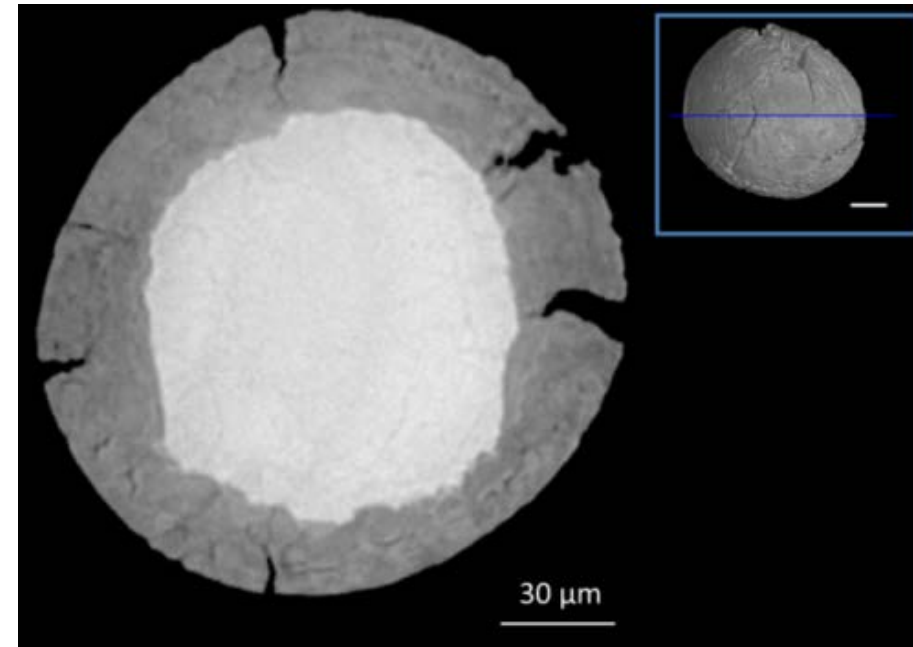
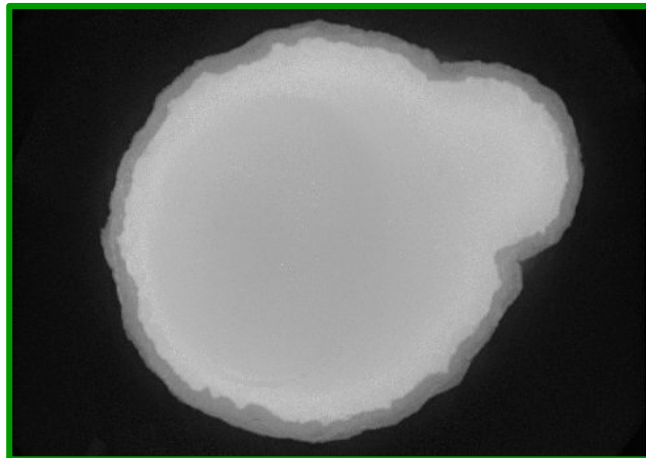
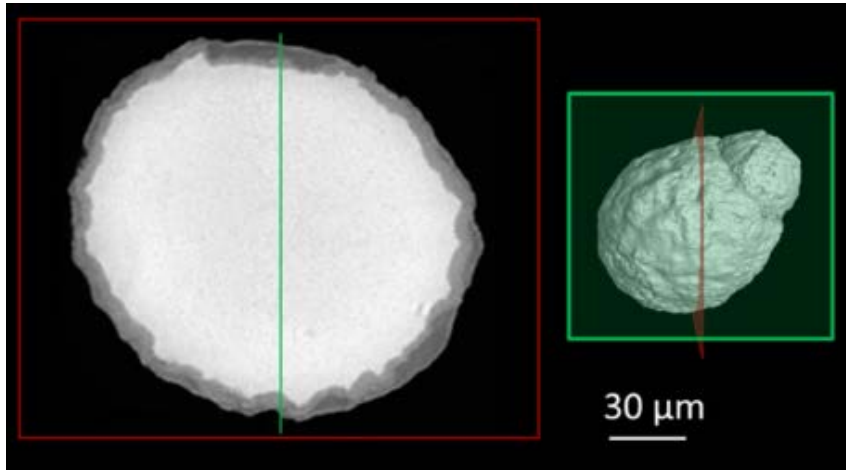
H. Palancher *et al.*, *J. Appl. Cryst.* (2012). **45**, 906-913

Method firstly validated on 0,4 μm thick ZrN coated U-Mo particles using FIB/SEM (INL measurements)

T. Zweifel *et al.*, *J. Nucl. Mater.* (2013). **442**, 124-132.

## The UMo(N) case

Phases from the coating represent more than 37 wt% of the material which is not consistent with a 2-3 μm thick layer measured with SEM: N diffusion deep into UMo particles has damaged the U-Mo long-range crystallinity

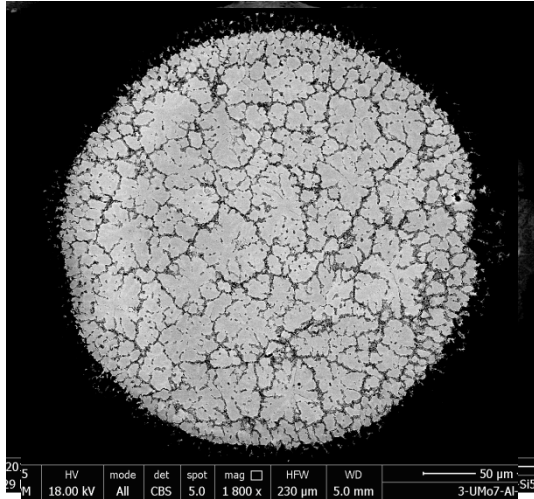


$\mu$ -CT helps evidencing:

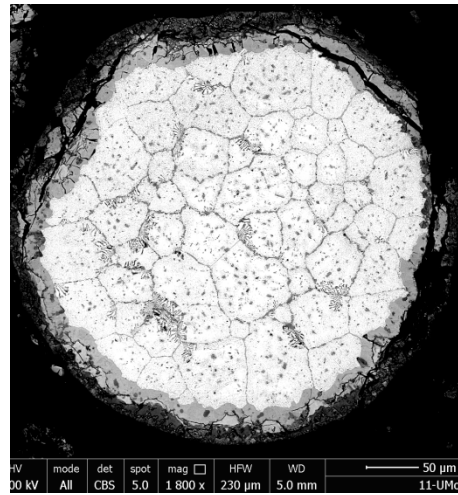
- The good quality of the coating even around particles with non-spherical shapes
- cracks that can not be due to sample preparation contrary to SEM for example.

# U-MO MICROSTRUCTURE EVOLUTION AFTER MEAT EXTRUSION AND TT : SEM AND HE-XRD ANALYSES

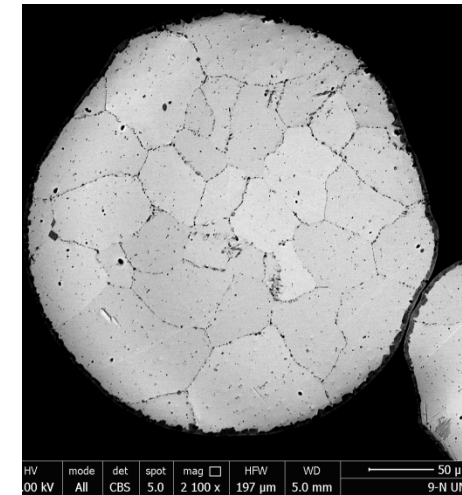
U-Mo(Si)/Al, Si5



U-Mo(Si)/Al  
(1000°C 1h)



U-Mo(N)/Al  
(1000°C 6h)



## SEM examinations:

much higher destabilization of the  $\gamma$ UMo phase (starting at grain boundaries) in U-Mo(Si)/Al than in U-Mo(N)/Al

## HE-XRD:

	U-Mo/Al	U-Mo(Si)/Al	U-Mo(N)/Al
Destabilisation ratio	15.1	23.7	2.1

**Good agreement between both analyses !!!**



# CONCLUSIONS

A wide range of cutting edge measurements have been performed to investigate both the coating and the microstructure of U-Mo particles

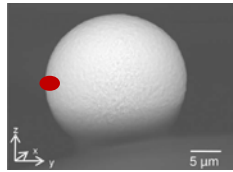
	As-atomised U-Mo	U-Mo(Si) (1000°C 1h)	U-Mo(N) (1000°C 6h)
Average grain size ( $\mu\text{m}$ )	<6	15	17
Grain shape	dendritic	Sharpe edges	<ul style="list-style-type: none"> <li>• Sharpe edges</li> <li>• Some « single crystal particles »</li> </ul>
Consequences of the coating	---	<ul style="list-style-type: none"> <li>• Precipitation of Mo, Si, O</li> <li>• High oxygen pollution</li> </ul>	Lower long range order in U-Mo phase
Destabilisation ratio In the annealed meat	15	24	2

A wide range of cutting edge measurements have been performed to investigate both the coating and the microstructure of U-Mo particles

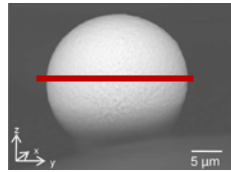
	As-atomised U-Mo	U-Mo(Si) (1000°C 1h)	U-Mo(N) (1000°C 6h)
Average grain size ( $\mu\text{m}$ )	<6	15	17
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Consequences of the coating	---	<ul style="list-style-type: none"> <li>• Precipitation of Mo, Si, O</li> <li>• High oxygen pollution</li> </ul>	Lower long range order in U-Mo phase
Destabilisation ratio In the annealed meat	15	24	2
Coating crystallographic composition	---	Composed of wide range of crystallographic phases	Mainly UN
Presence of cracks	---	Some particles with radial cracks	Too thin to exhibit large cracks

A. Bonnin, post-doc (2010-2012)

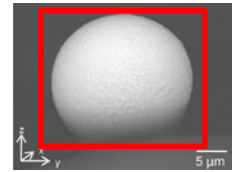
## Development of a non destructive approach for coating layers and their evolution at the different steps of the manufacturing process



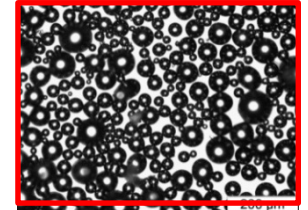
0.1 μm



0.1 μm



20-120 μm



~ cm<sup>2</sup>



Nano-XRD

Nano XRD-CT

Far field 3D-XRD

HE-XRD

Crystallographic composition:

×

×

×

×

Thickness:

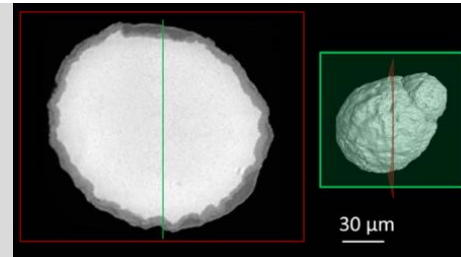
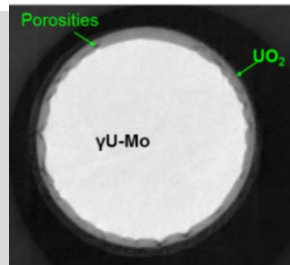
×

×

×

×

Other coating characteristics (Density, shape, coating/core interface)

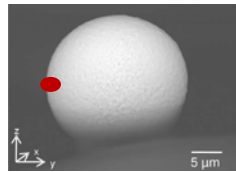


HE-μCT

×

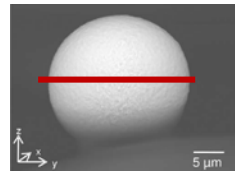
A. Bonnin, post-doc (2010-2012)

## As-atomised U-Mo particle microstructure



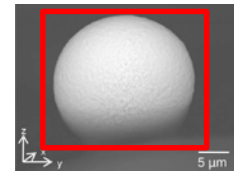
0.1 μm

Nano-  
XRD



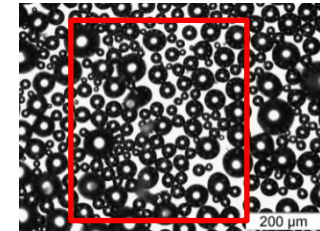
0.1 μm

Nano  
XRD-CT



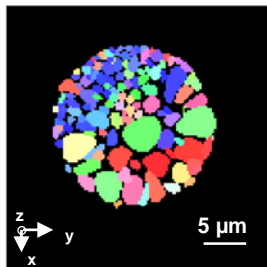
20-120 μm

Far field 3D-  
XRD

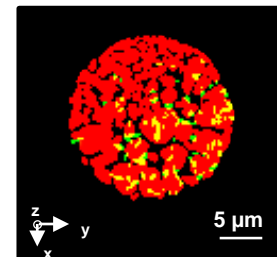


~ cm<sup>2</sup>

HE-XRD



- U-Mo grain orientation map
- U(C, O) grain map and orientation relationships with U-Mo
- U(C,O) precipitates do not act as nucleation sites for U-Mo grains



- Two  $\gamma$ U-Mo lattice constants
- Additional tetragonal superlattice
- Quantification of impurities:  
 $U(C,O) = 1 \text{ wt.}\%$   
 $UO_2 = 0.3 \text{ wt.}\%$



**THANK YOU FOR YOUR ATTENTION**