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

H. Palancher, X. Iltis, H. J. Ryu, K. H. Lee, Y. J. Jeong, J. M. Park, M. Delpech

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

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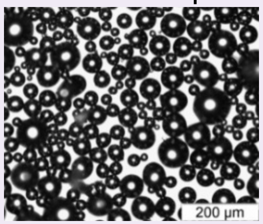
U-MO/AL SAMPLE MANUFACTURING (NO-CLADDING)

U-Mo Powder

Atomization

90<Ø<150 µm



Coating

Solid/gas reaction

Solid/solid reaction

U-Mo/Al Compact

Powder blending

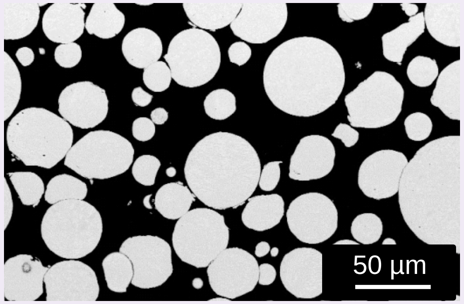
Compaction

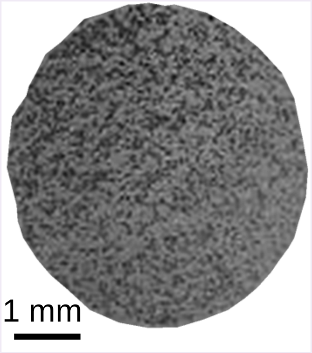
Extrusion

T < 450°C
Duration ≈ 1h

As-fabricated fuel meat

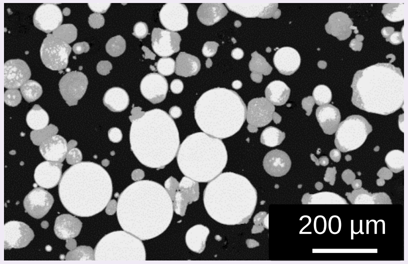
Upper view





Post-manufacturing annealing

Temperature: 580°C
Duration: 1h



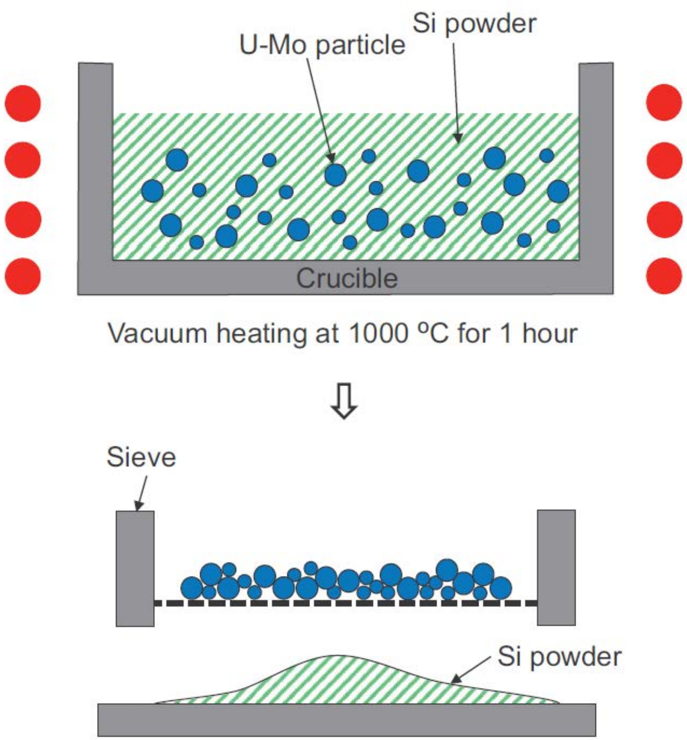
W.J. Kim *et al*., J. of Alloys and Compds 589 (2014) 94–100.

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

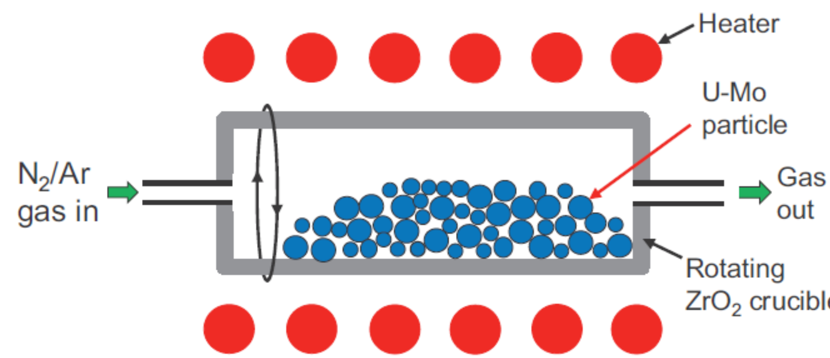
H.J. Ryu et al., Nucl. Eng. Technol. 43 (2011) 159-166.

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

Si coating



Nitride coating



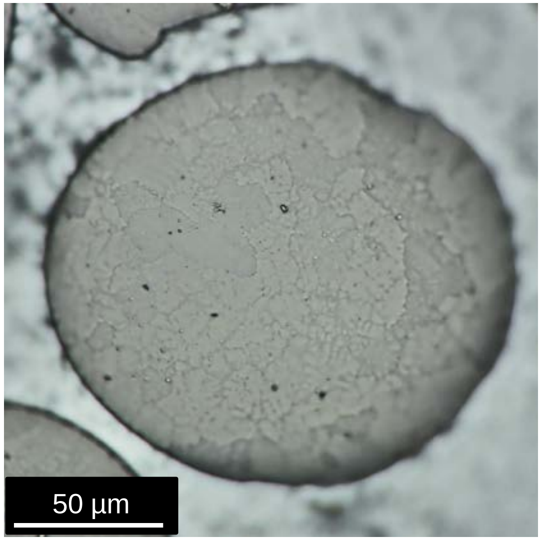
The operation conditions of nitride coating.

Parameters	Conditions
Back ground pressure	1×10^{-6} torr
Working pressure	3×10^{-5} torr
N_2-gas flow	80 sccm
Revolution speed	30 rpm
Temperature	1000 °C
Holding time	
U–7 wt%Mo	6 h
U–7 wt%Mo–1 wt%Ti	1–4 h

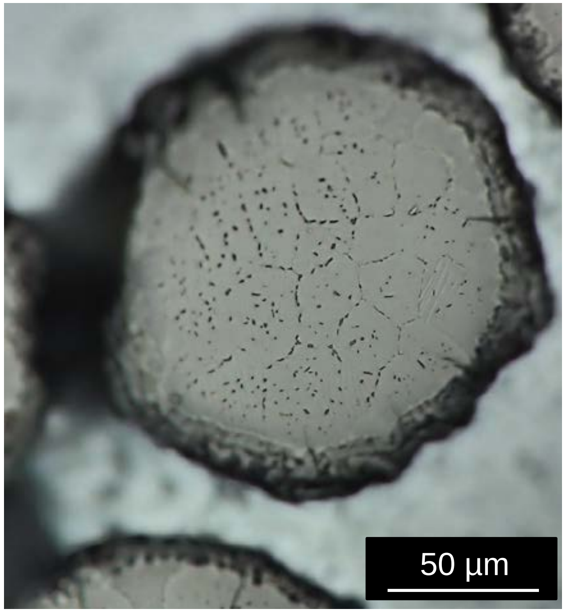
Goals of the characterisation: coating composition but also U-Mo grain size modification

GRAIN SIZE EVALUATION USING OPTICAL MICROSCOPY

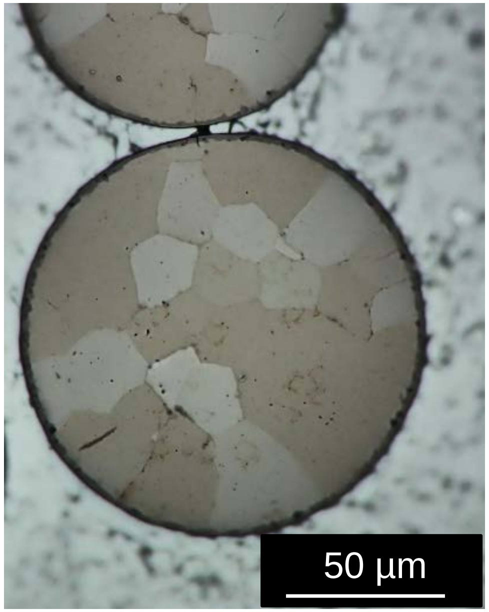
As-atomised



U-Mo(Si)
(1000°C 1h)

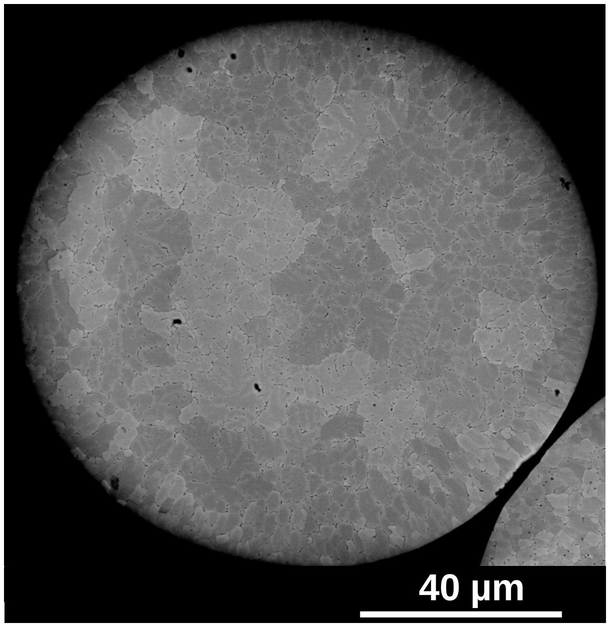


U-Mo(N)
(1000°C 6h)

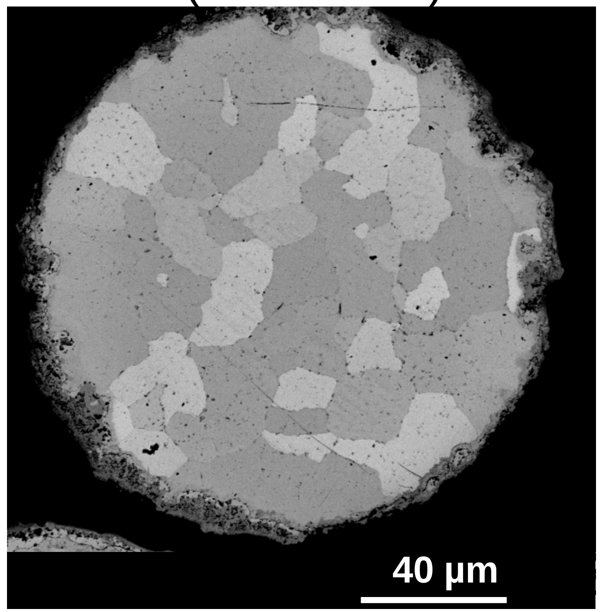


GRAIN SIZE EVALUATION USING SEM

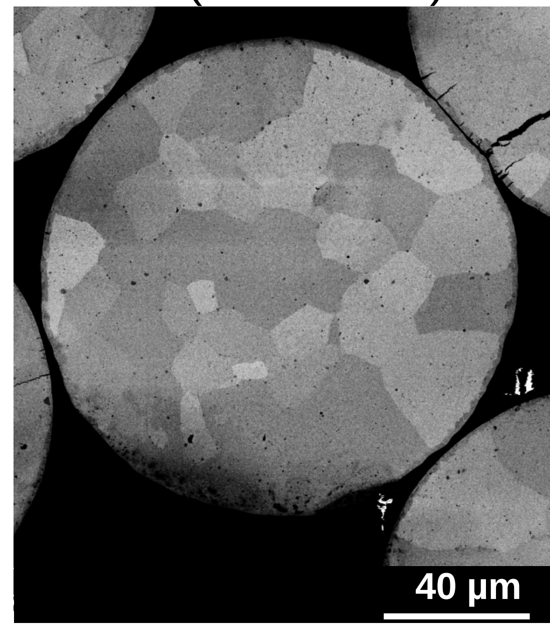
As-atomised

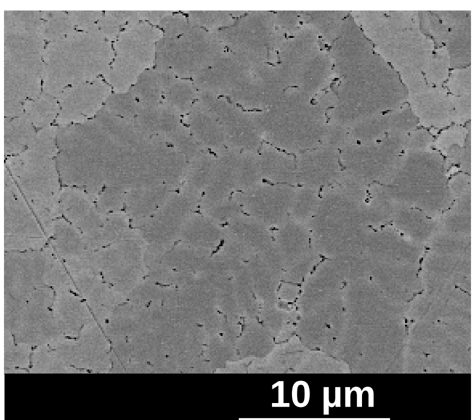


U-Mo(Si)
(1000°C 1h)



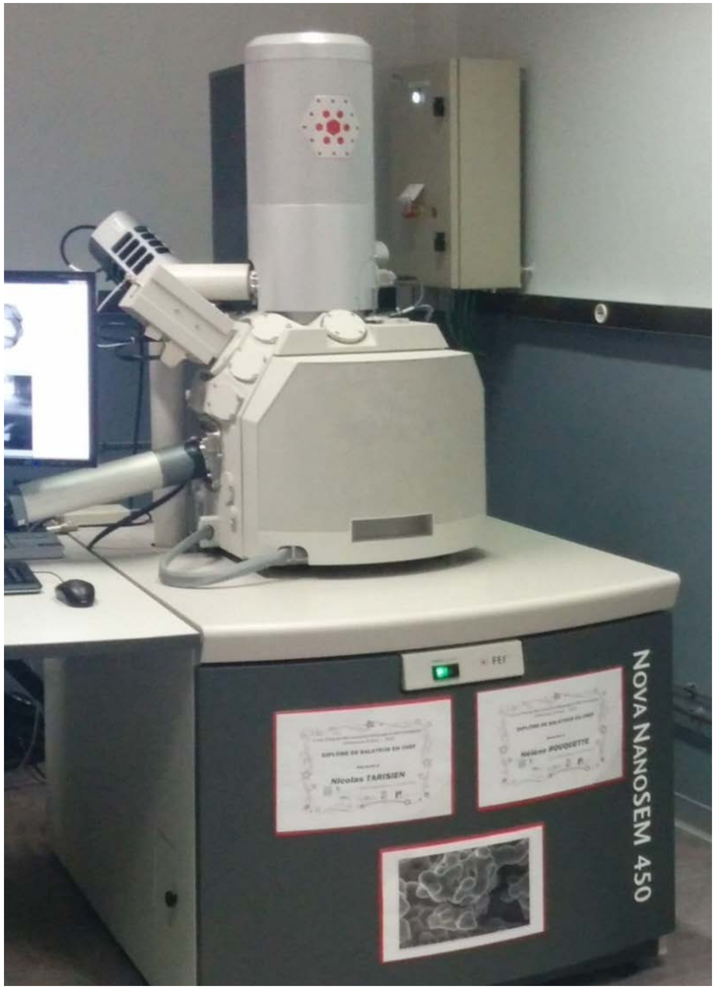
U-Mo(N)
(1000°C 6h)

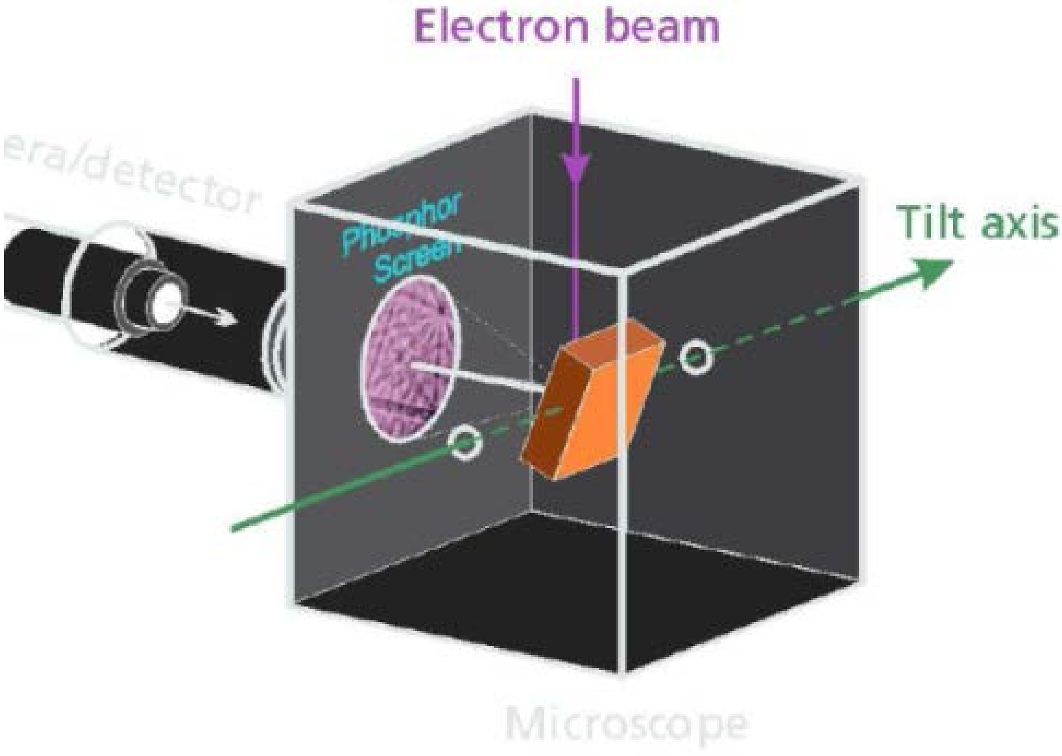




Even with high quality SEM characterisation combined with image analysis, grain size is difficult to determine accurately.

ELECTRON BACK-SCATTER DIFFRACTION (EBSD)

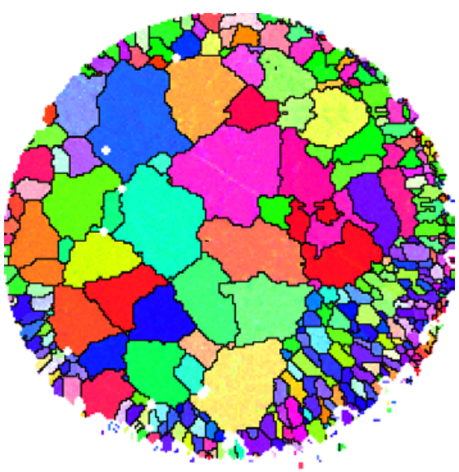




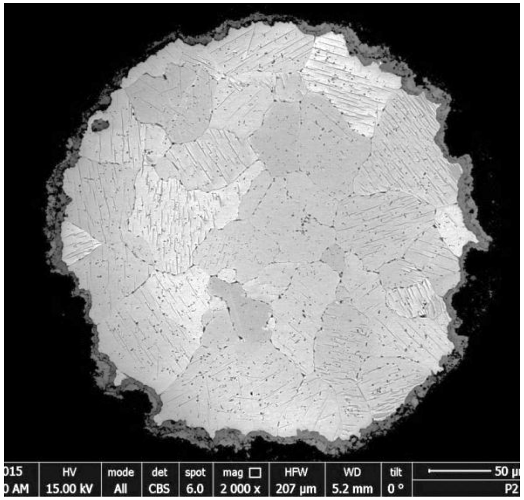
For further technical details on the application of this technique on as-atomised UMo nuclear fuel:
See: ***G. Champion, Ph.D. Thesis (Rennes University) 2013 (France).***

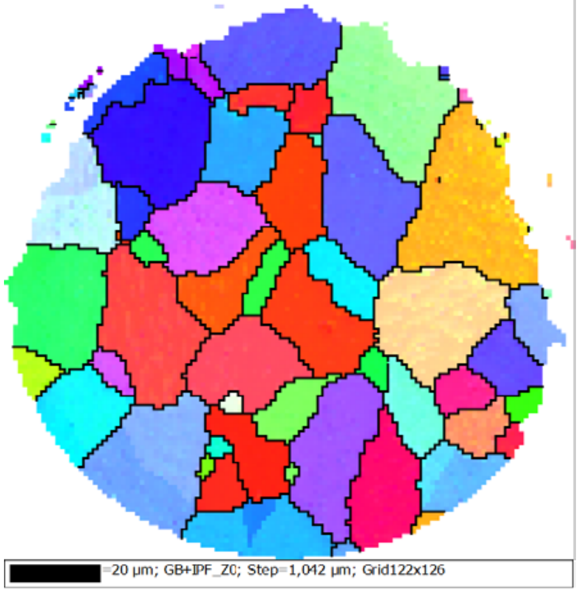
GRAIN SIZE EVALUATION USING EBSD (I/II)

As-atomised

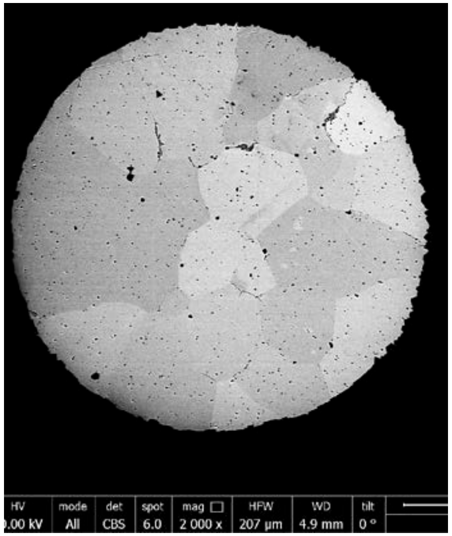


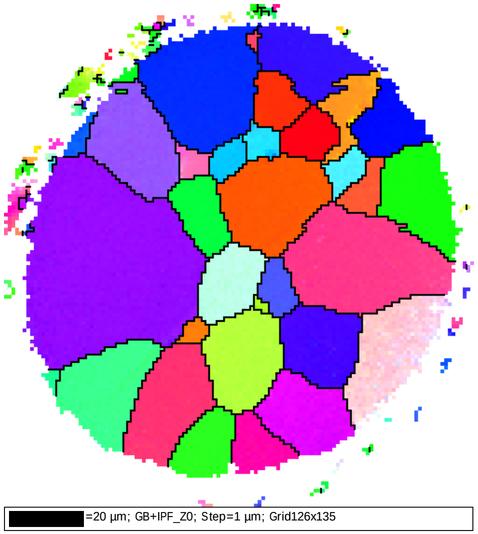
U-Mo(Si) (1000°C 1h)



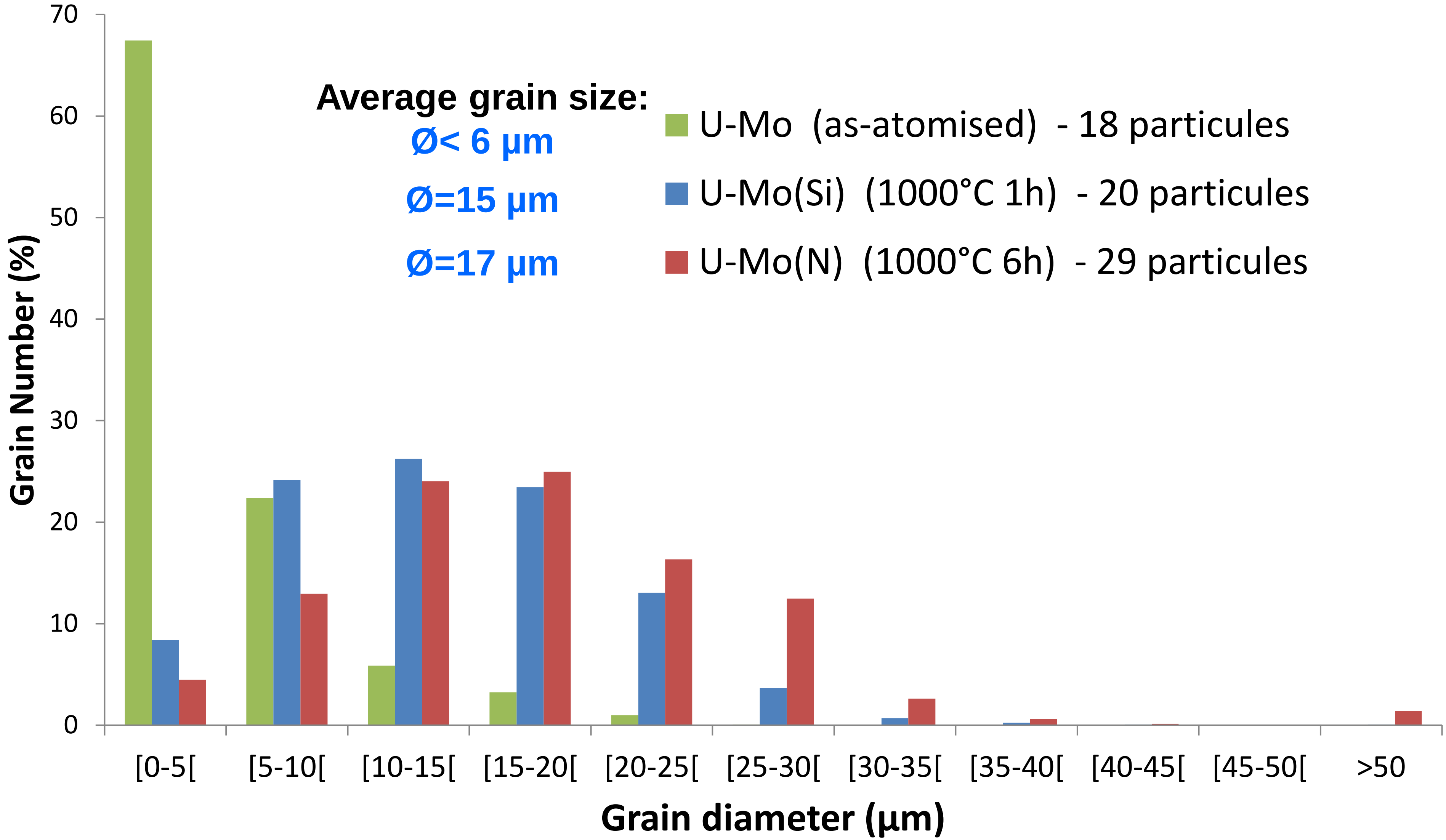


U-Mo(N) (1000°C 6h)



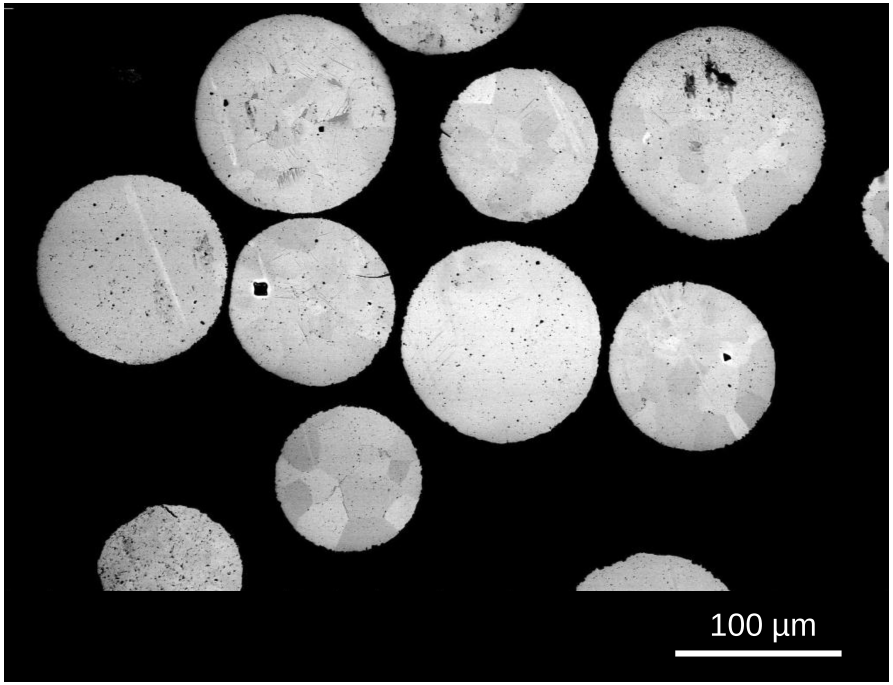


GRAIN SIZE EVALUATION USING EBSD (II/II)

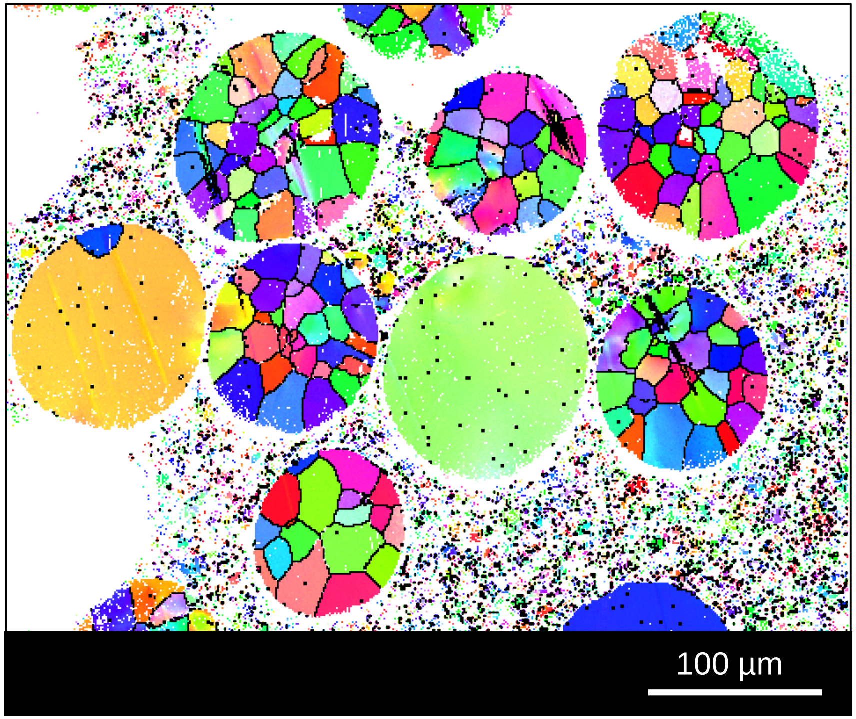


U-MO MICROSTRUCTURE AFTER TT AT 1000°C DURING 6H: LARGE EBSD MAPS

SEM



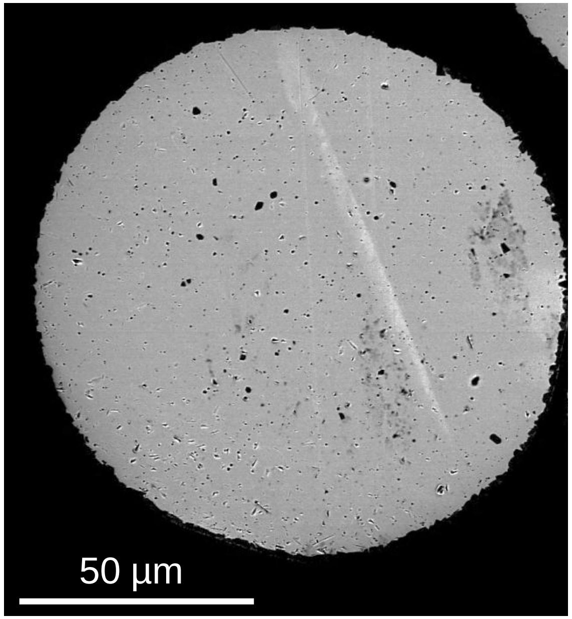
EBSD



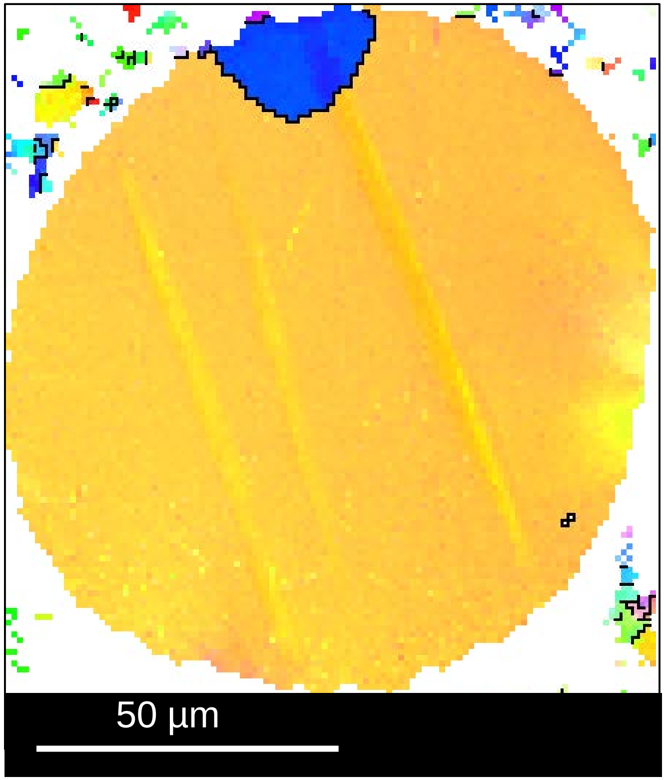
Evidence for the presence of « single crystal » U-Mo particles

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

SEM

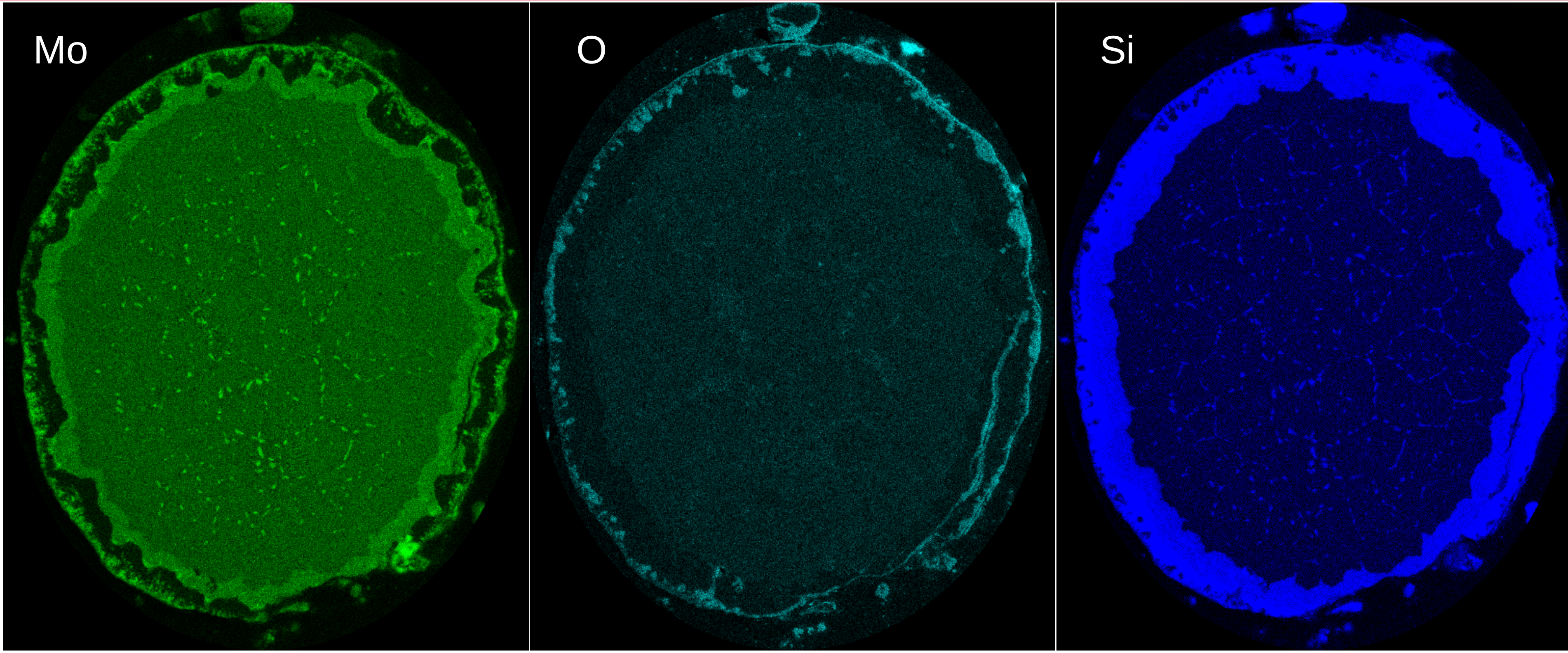


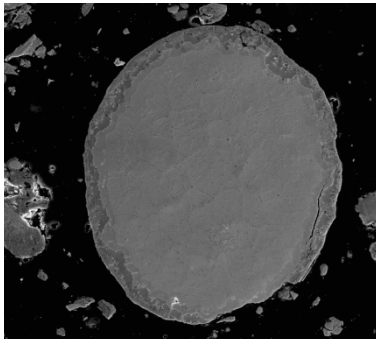
EBSD



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

PRECIPITATION AS A RESULT OF THE POWDER ANNEALING

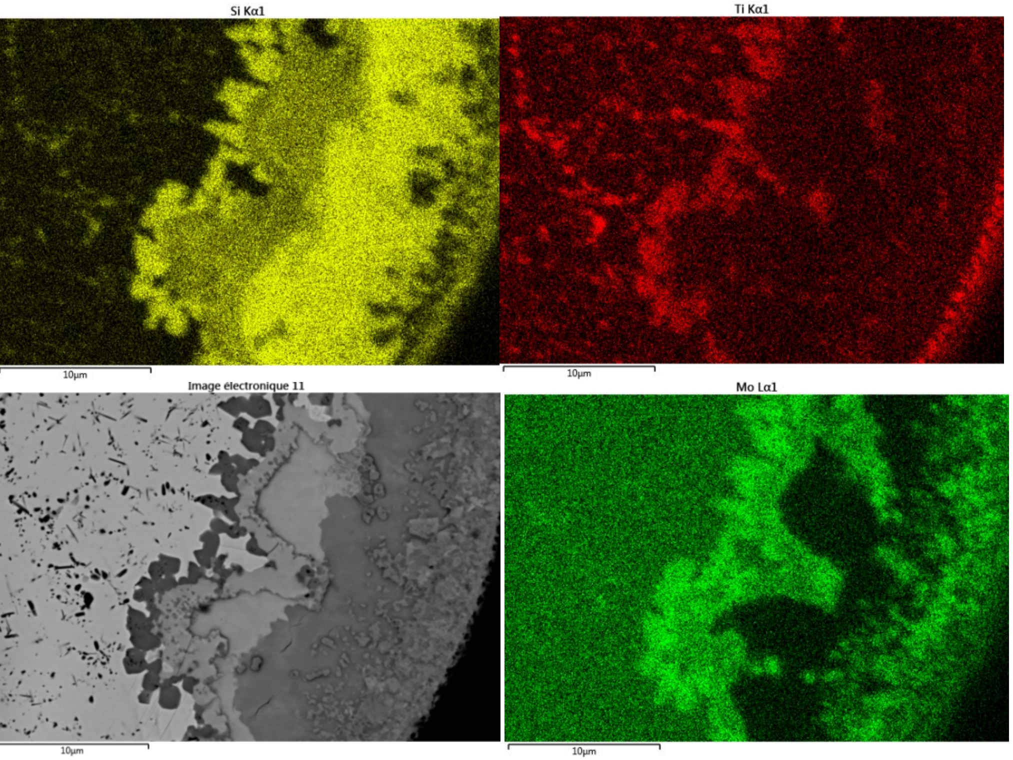




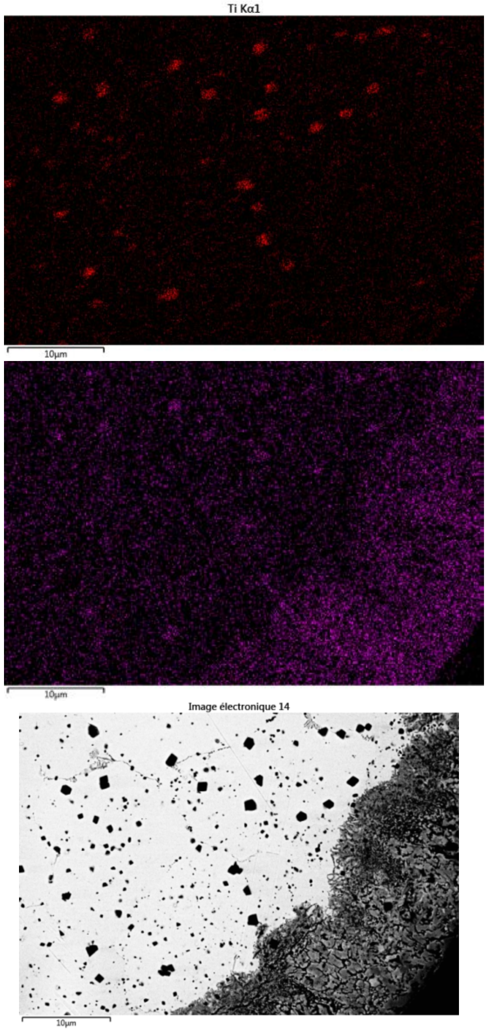
In U-Mo (Si) particles, intergranular Mo-Si rich precipitates can be observed

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

U-Mo-Ti(Si)
(1000°C 1h)



U-Mo-Ti (N)
(1000°C 6h)



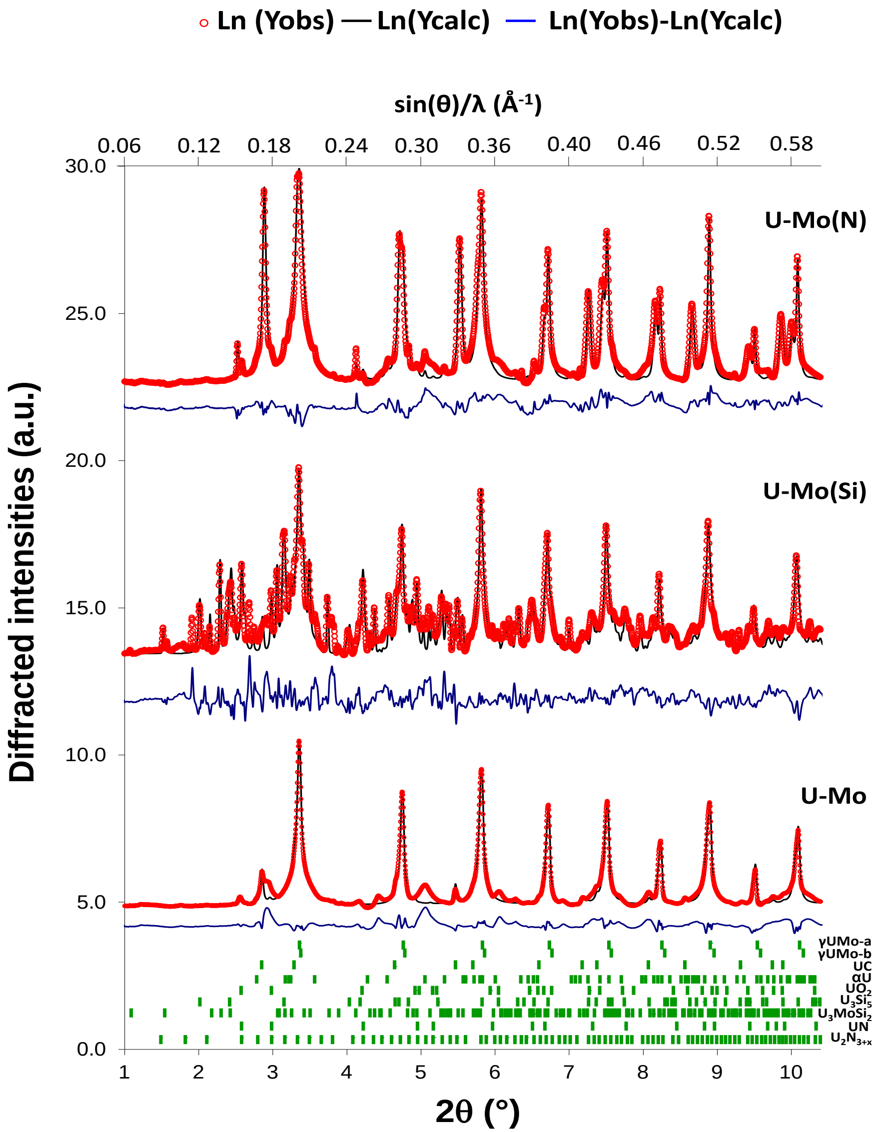
Ti

N

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)



ID15B@ESRF

- Two γU-Mo lattice constants in the as-atomised case only
- Additional tetragonal superlattice
- Quantification of impurities:
  - U(C,O)
  - UO_2

X-RAY DIFFRACTION AT HIGH ENERGY (87 KEV)

	Weight fraction (%									
	U-Mo core			Pollution	N Coating		Si coating			
	γ-UMo	α-U	UC	UO_2	UN	U_4N_7	$USi_{1.88}$	U_3Si_2	U_3Si_5	U_3MoSi_2
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

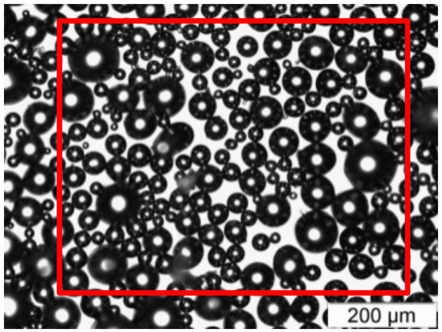
Conclusion :

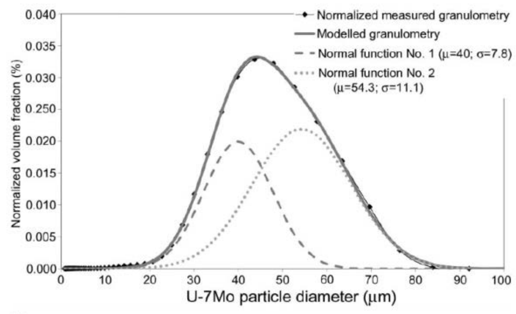
- No destabilization of the γU-Mo phase (cooling rate high enough)
- Very high concentration of UN phase in U-Mo(N) (not consistent with 2-3 µm thick coating)
- Very complex crystallographic composition of the UMo(Si) coating

	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

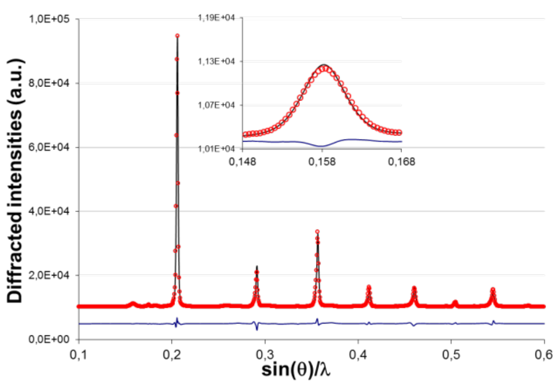
HE-XRD measurements on **powder sample**





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

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



Validation of the method

Method firstly validated on 1 µm thick UO_2 coated U-Mo particles using tomography

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

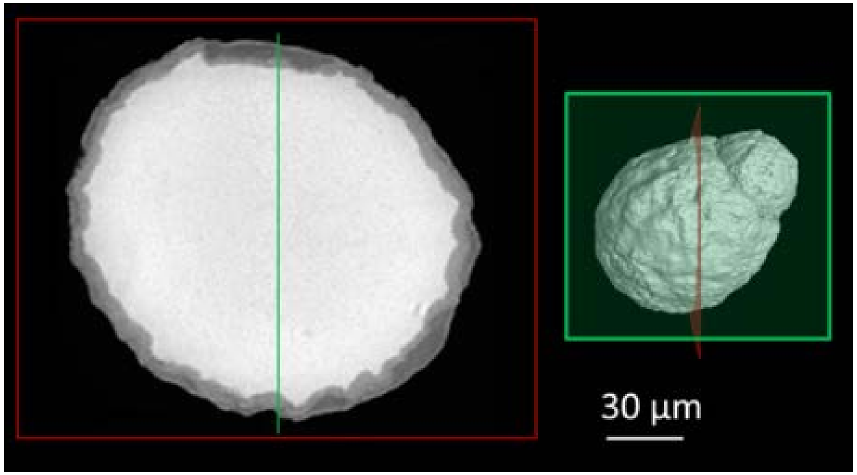
Method firstly validated on 0,4 µm thick ZrN coated U-Mo particles using FIB/SEM (INL measurements)

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

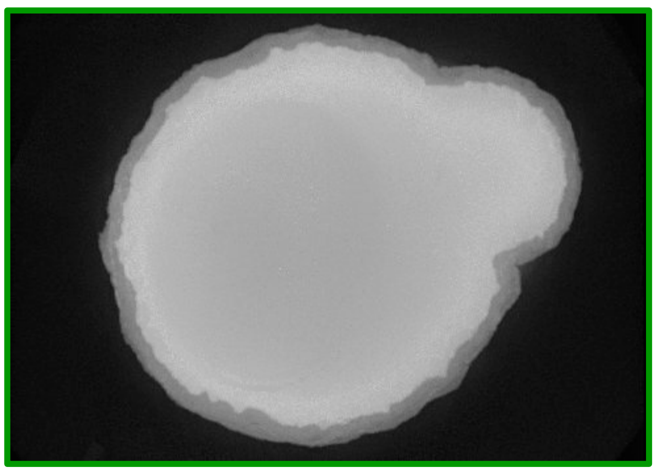
The UMo(N) case

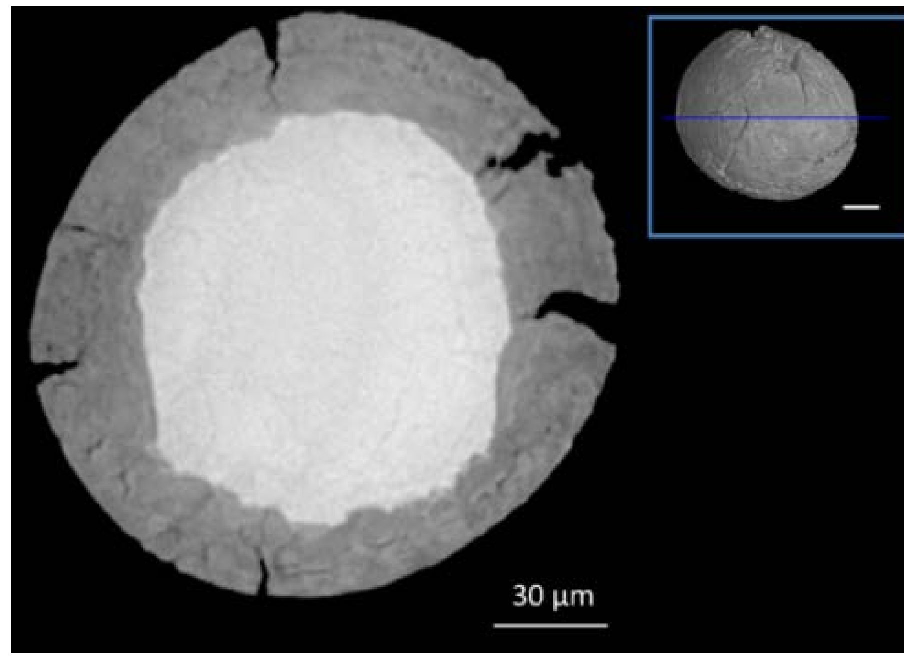
Phases from the coating represent more than 37 wt% of the material which is not consitent with a 2-3 µm thick layer measured with SEM: N diffusion deep into UMo particles has damaged the U-Mo long-range crisytallinity

COATING: HE-MCT ON U-MO(SI)



ID19@ESRF
Coll. A. Bonnin



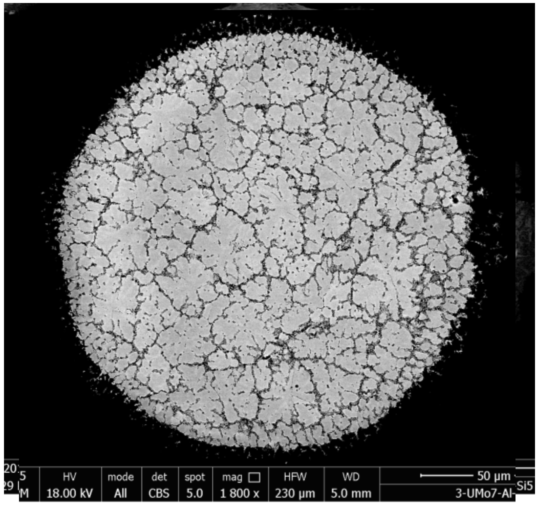


µ-CT helps evidencing:

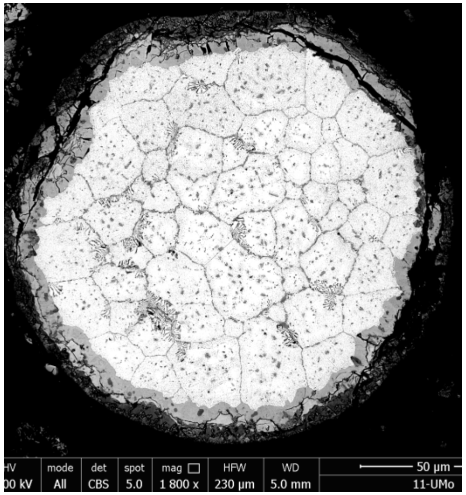
- The good quality of the coating even around particles with non-spherical shapes
- cracks that can not be due to sample preparation contrary to SEM for example.

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

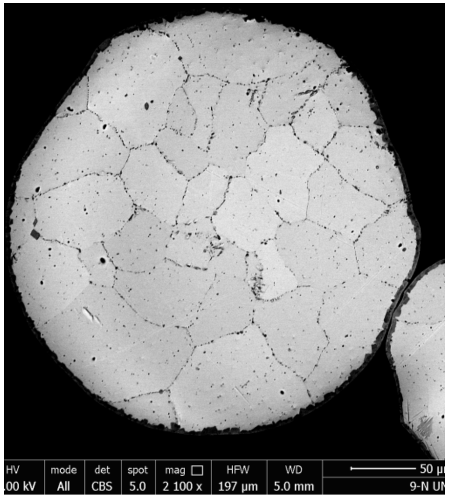
U-Mo(Si)/Al,Si5



U-Mo(Si)/Al
(1000°C 1h)



U-Mo(N)/Al
(1000°C 6h)



SEM examinations:

much higher destabilization of the γUMo 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 (µm)	<6	15	17
Grain shape	dendritic	Sharpe edges	• Sharpe edges • Some « single crystal particles »
Consequences of the coating	---	• Precipitation of Mo, Si, O • High oxygen pollution	Lower long range order in U-Mo phase
Destabilisation ratio In the annealed meat	15	24	2

CONCLUSIONS

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

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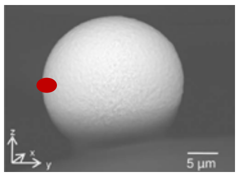
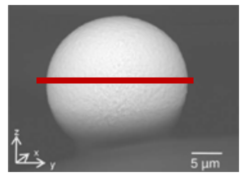
Consequences of the coating	---	• Precipitation of Mo, Si, O • High oxygen pollution	Lower long range order in U-Mo phase
Destabilisation ratio In the annealed meat	15	24	2
Coating crystallographic composition	---	Composed of wide range of crystallographic phases	Mainly UN
Presence of cracks	---	Some particles with radial cracks	Too thin to exhibit large cracks

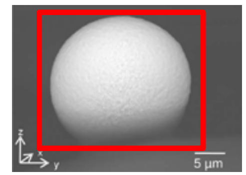
3D MULTI SCALE ANALYSIS OF COATINGS USING SYNCHROTRON RADIATIONS

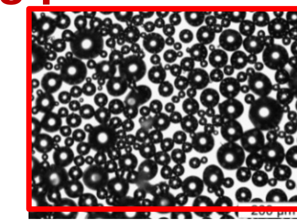
A. Bonnin, post-doc (2010-2012)

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

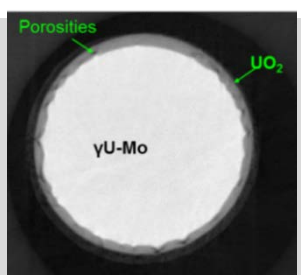
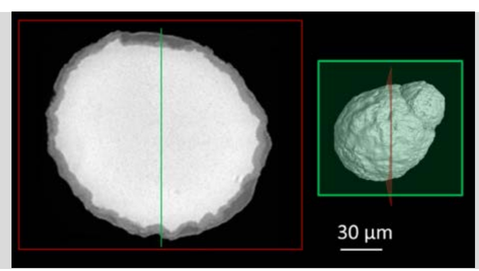








X-ray beam size	0.1 µm	0.1 µm	20-120 µm	~ cm²

	Nano-XRD	**Nano XRD-CT**	**Far field 3D-XRD**	**HE-XRD**
Crystallographic composition:	×	×	×	×
Thickness:	×	×	×	×
Other coating characteristics (Density, shape, coating/core interface)				**HE-µCT** ×

M. Stockmar *et al.*, Phys. Rev. Applied **3** (2015), 014005

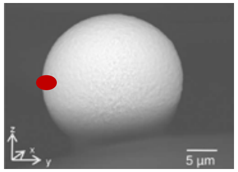
H. Palancher *et al.*, *J. Appl. Cryst.* (2012). **45**, 906-913

3D MULTI SCALE ANALYSIS USING SYNCHROTRON RADIATIONS

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

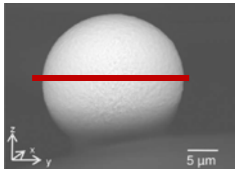
As-atomised U-Mo particle microstructure

A light for science ESRF



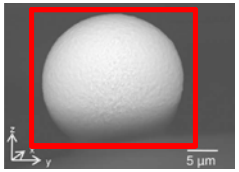
0.1 µm

Nano-XRD



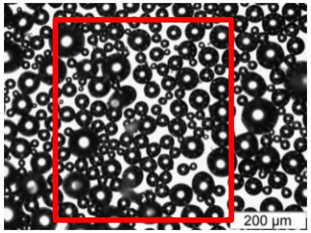
0.1 µm

Nano XRD-CT



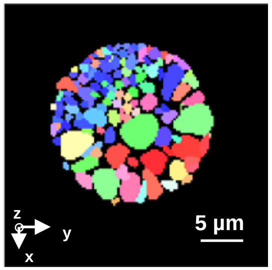
20-120 µm

Far field 3D-XRD

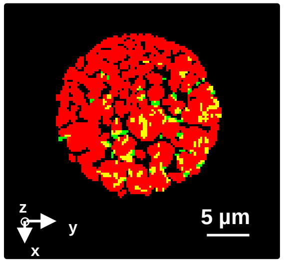


~ cm²

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 γU-Mo lattice constants**
- **Additional tetragonal superlattice**
- **Quantification of impurities:**
  U(C,O) =1 wt.%
  UO_2 =0.3 wt.%

A. Bonnin, J. Wright, R. Tucoulou, H. Palancher, Appl. Phys. Lett. **105** (2014), 084103.

THANK YOU FOR YOUR ATTENTION