



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

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

H. Palancher, X. Iltis

CEA, DEN, DEC, F-13108 Saint Paul Lez Durance Cedex – France

H.J. Ryu



Korea Advanced Institute of Science and Technology, 291
Daehakro, Yuseong, Daejeon 305-701 - Republic of Korea

K.H. Lee, Y.J. Jeong, J.M Park

Research Reactor Fuel Development Division
Korea Atomic Energy Research Institute, 989-111 Daedeokdaero,
Yuseong, 305-353 Daejeon – Republic of Korea



M. Delpech

CEA, DEN, DISN, 91191 Gif sur Yvette– France

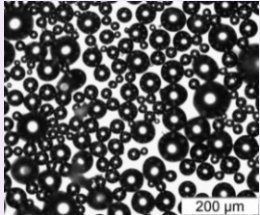
U-MO/AL SAMPLE MANUFACTURING (NO-CLADDING)



U-Mo Powder

Atomization

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



Coating

Solid/gas reaction
Solid/solid reaction



U-Mo/Al Compact

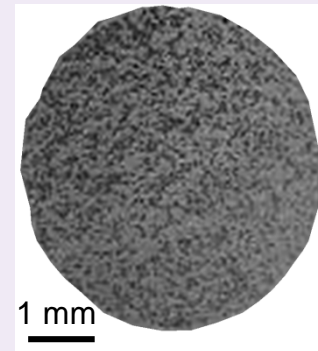
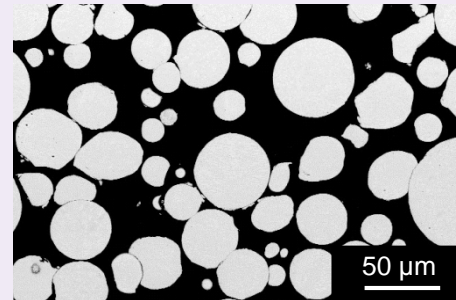
Powder blending
Compaction

Extrusion

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

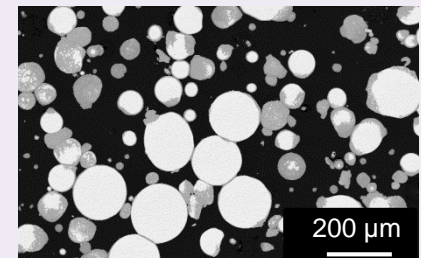
As-fabricated fuel meat

Upper view



Post-manufacturing annealing

Temperature: 580°C
Duration: 1h

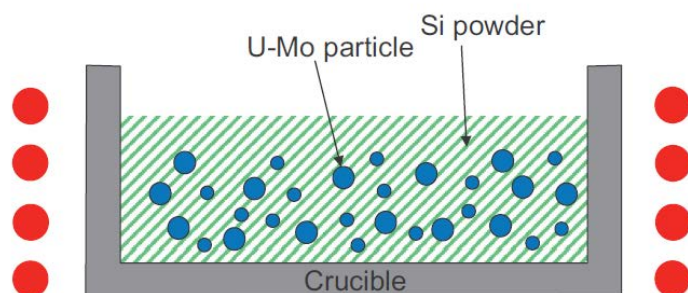


W.J. Kim *et al.*, J. of Alloys and Comps 589 (2014) 94–100.

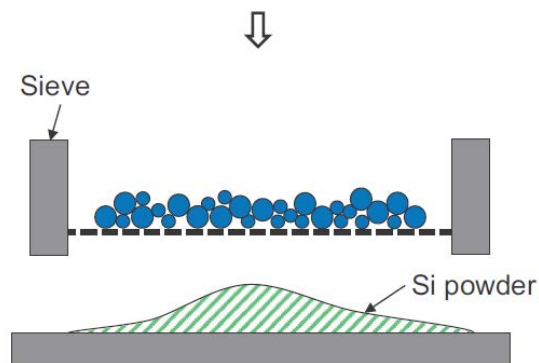
COATING CONDITIONS FOR THE U-MO POWDER (KOMO-5 TEST)

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

Si coating

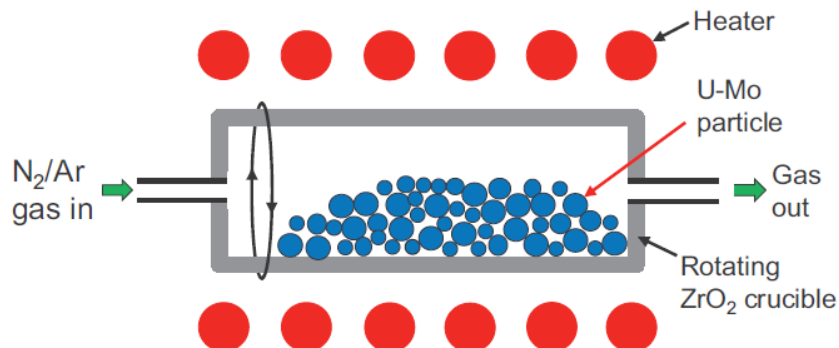


Vacuum heating at 1000 °C for 1 hour



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

Nitride coating



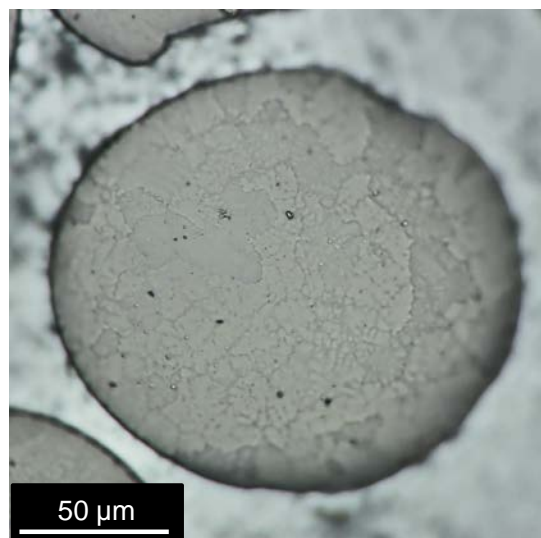
The operation conditions of nitride coating.

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
<i>Holding time</i>	
U-7 wt%Mo	6 h
U-7 wt%Mo-1 wt%Ti	1-4 h

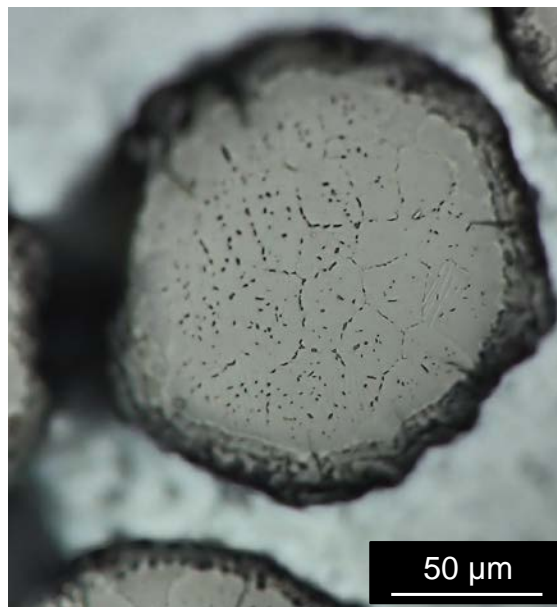
Goals of the characterisation: coating composition but also U-Mo grain size modification

GRAIN SIZE EVALUATION USING OPTICAL MICROSCOPY

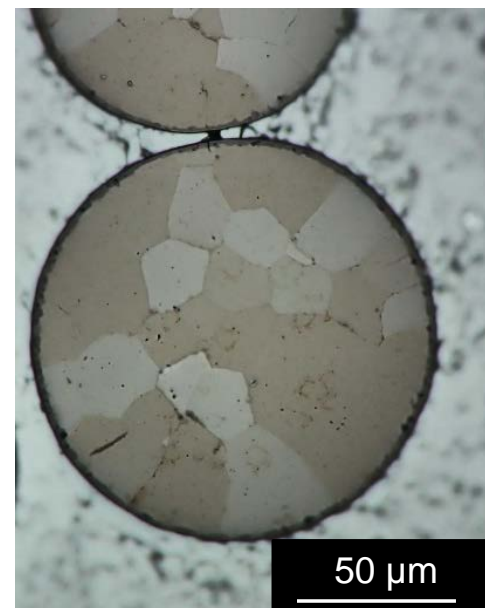
As-atomised



U-Mo(Si)
(1000°C 1h)

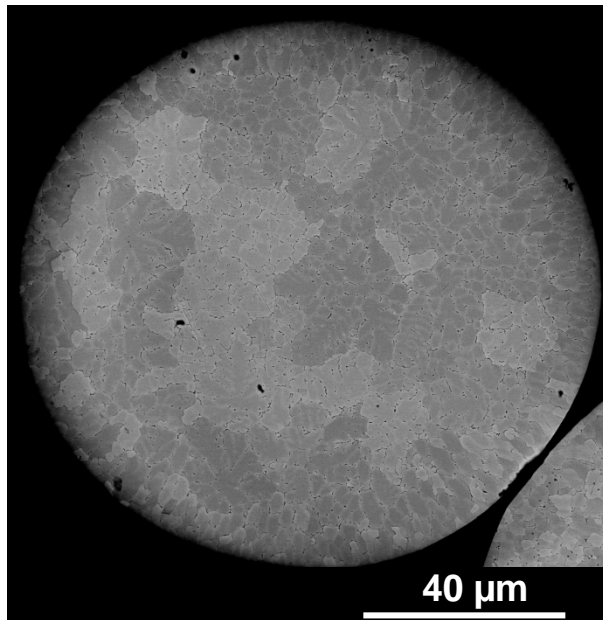


U-Mo(N)
(1000°C 6h)

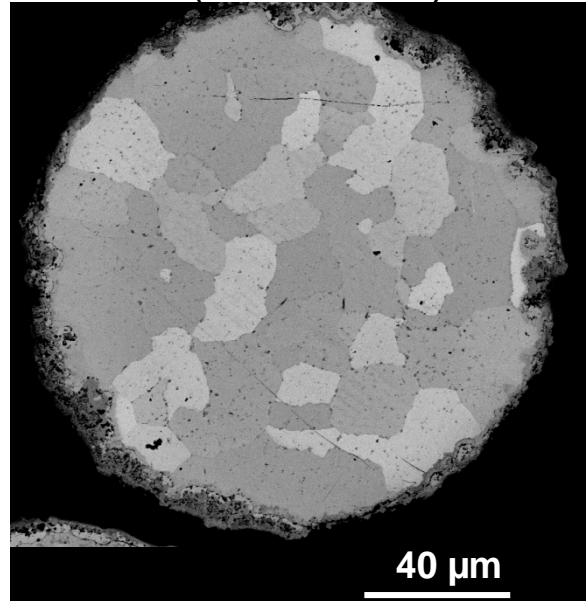


GRAIN SIZE EVALUATION USING SEM

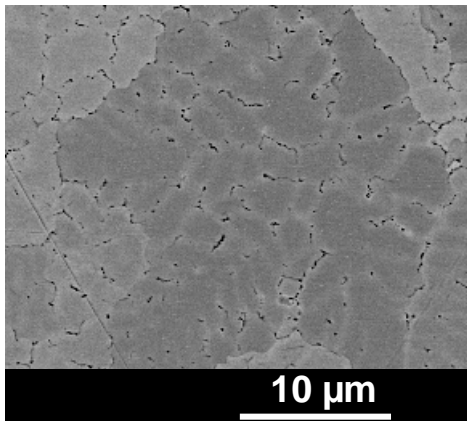
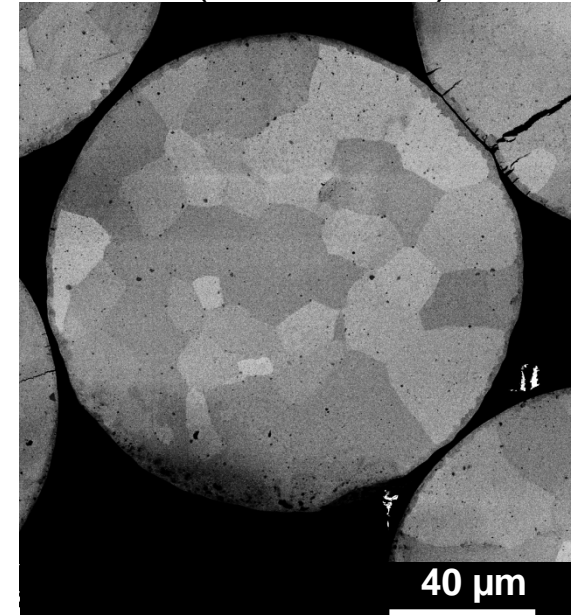
As-atomised



U-Mo(Si)
(1000°C 1h)

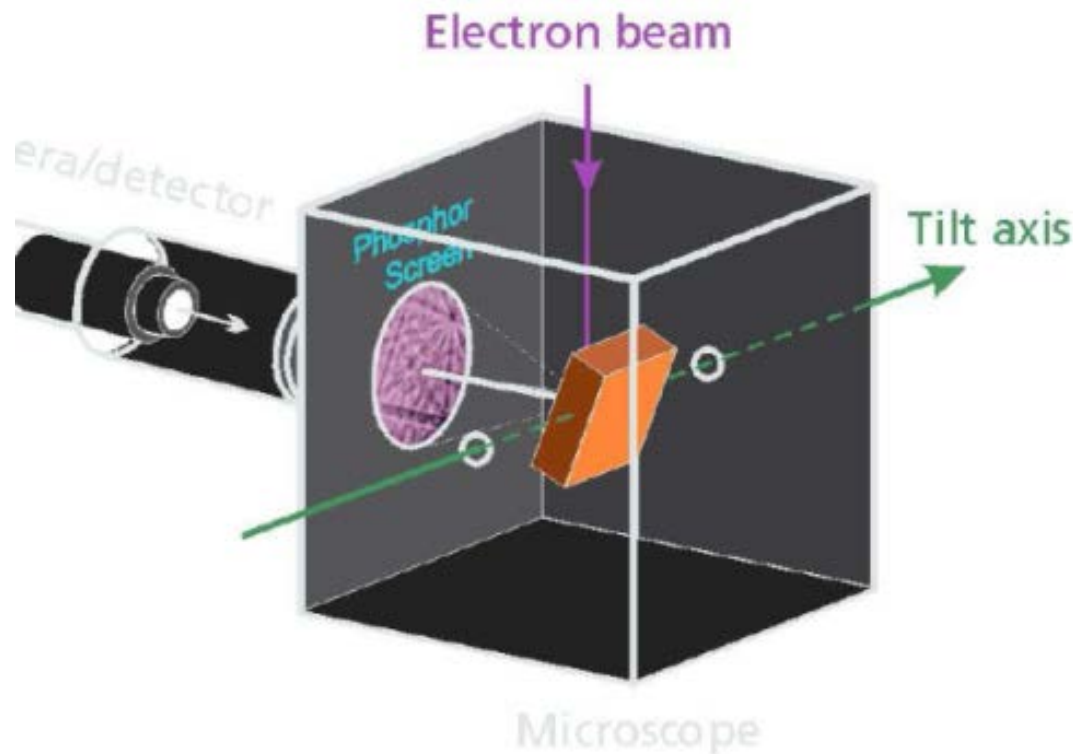
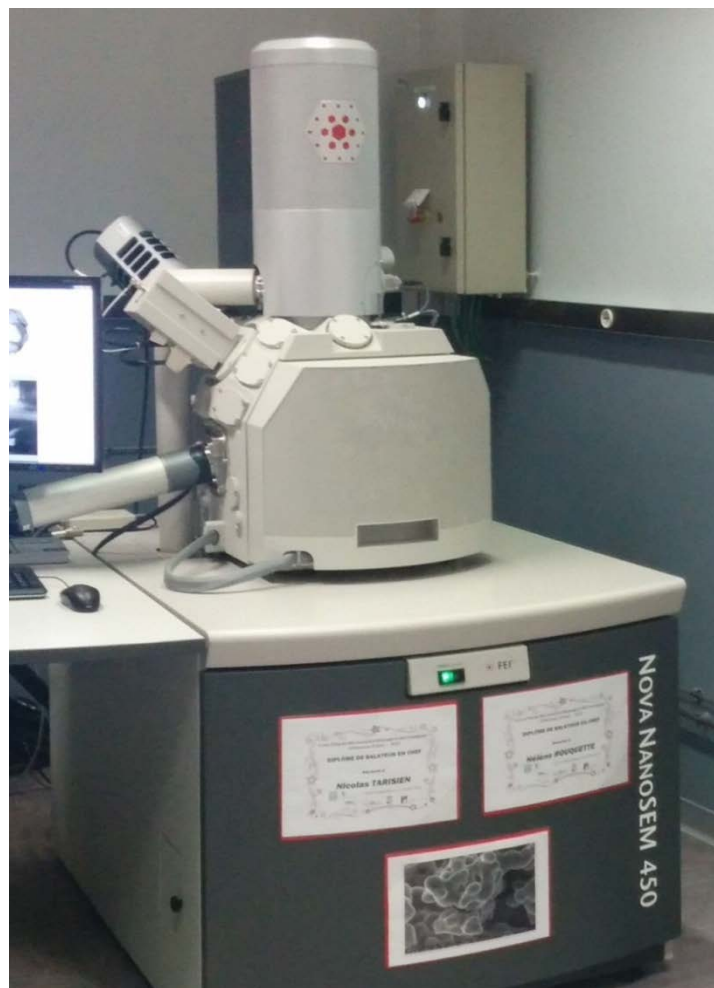


U-Mo(N)
(1000°C 6h)



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

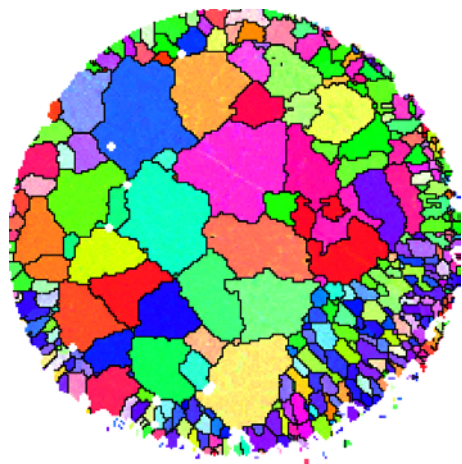
ELECTRON BACK-SCATTER DIFFRACTION (EBSD)



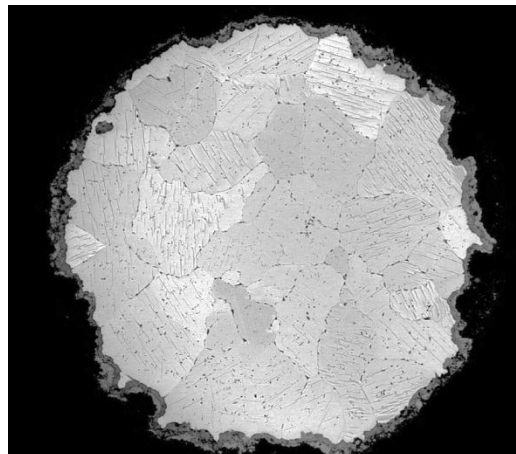
For further technical details on the application of this technique on as-atomised UMo nuclear fuel:
See: **G. Champion, Ph.D. Thesis (Rennes University) 2013 (France).**

GRAIN SIZE EVALUATION USING EBSD (I/II)

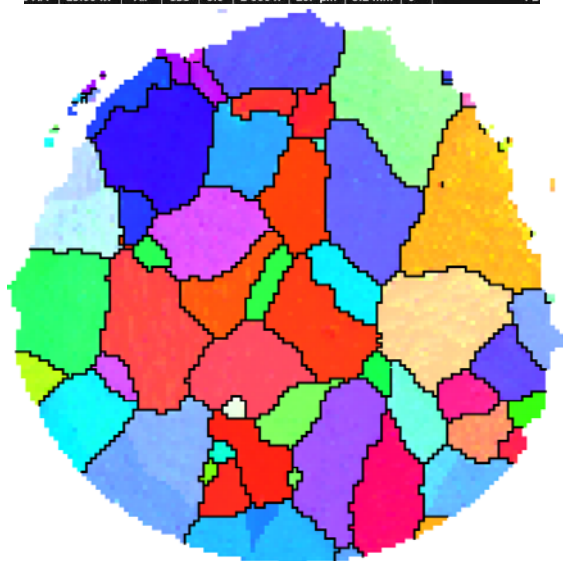
As-atomised



U-Mo(Si) (1000°C 1h)

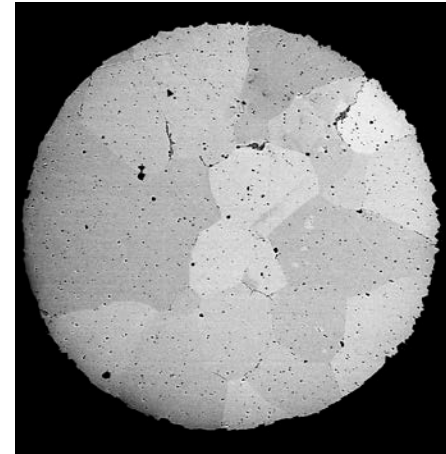


015 HV mode det spot mag HFW WD tilt
0 AM 15.00 kV All CBS 6.0 2 000 x 207 μm 5.2 mm 0 ° P2

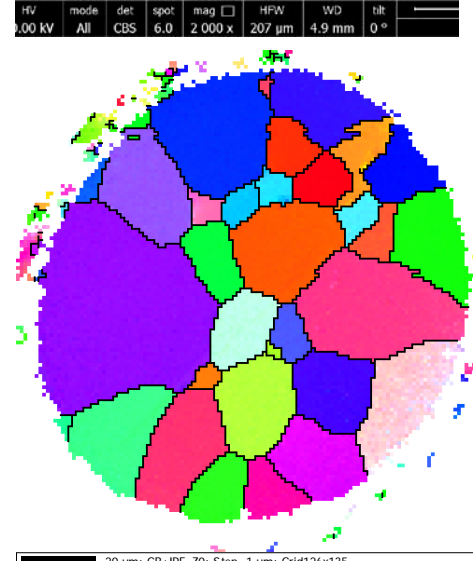


20 μm; GB+IPF_Z0; Step=1,042 μm; Grid122x126

U-Mo(N) (1000°C 6h)

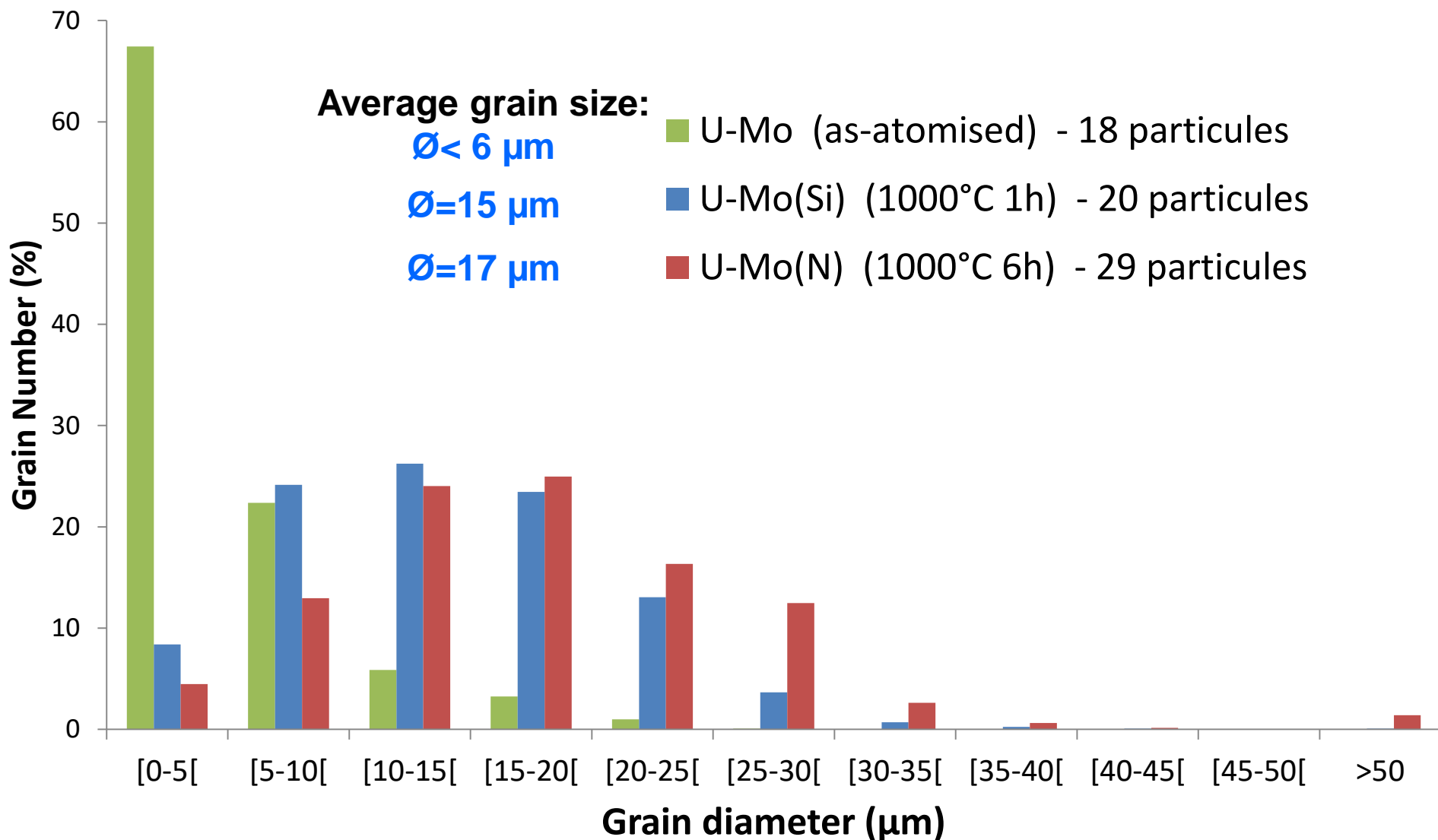


HV mode det spot mag HFW WD tilt
2.00 kV All CBS 6.0 2 000 x 207 μm 4.9 mm 0 °



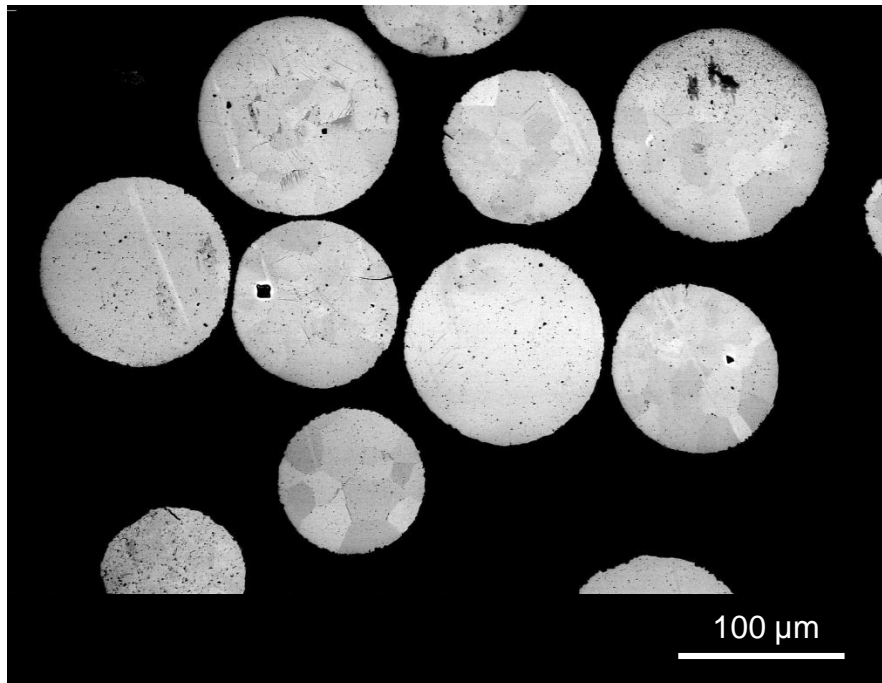
20 μm; GB+IPF_Z0; Step=1 μm; Grid126x135

GRAIN SIZE EVALUATION USING EBSD (II/II)

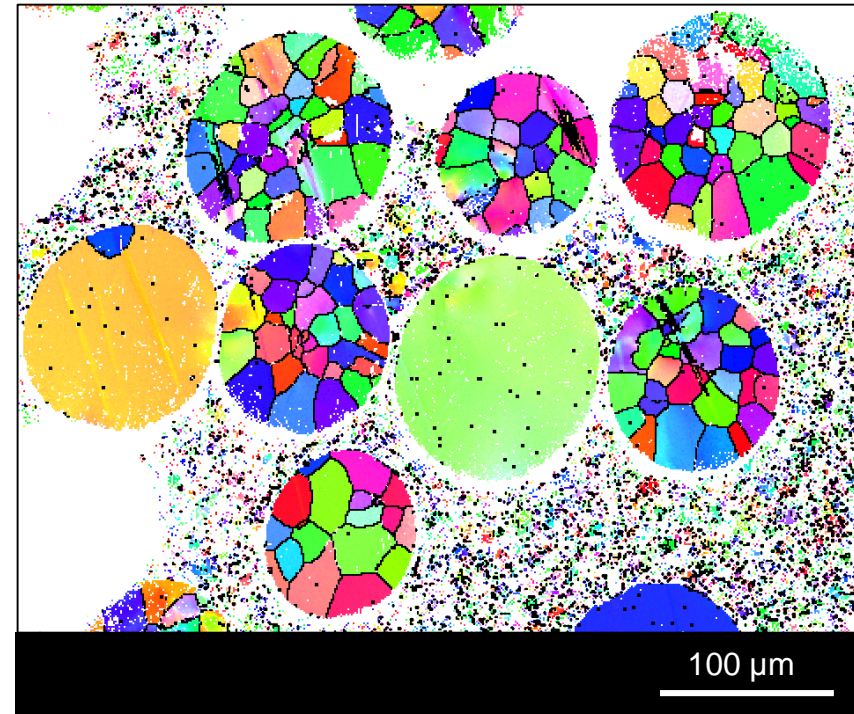


U-MO MICROSTRUCTURE AFTER TT AT 1000°C DURING 6H: LARGE EBSD MAPS

SEM



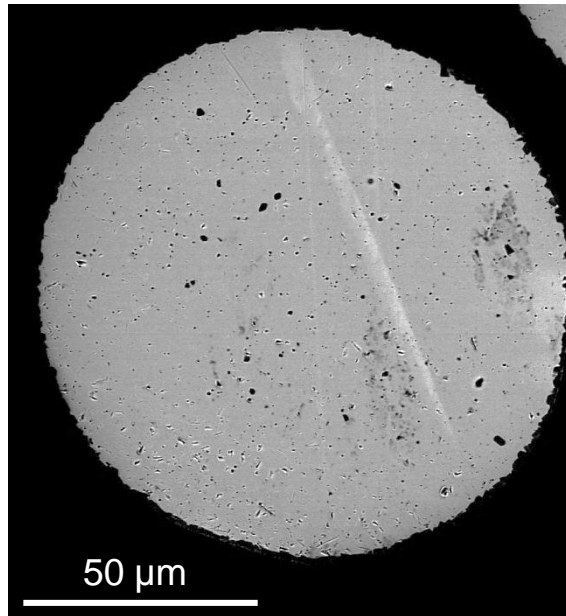
EBSD



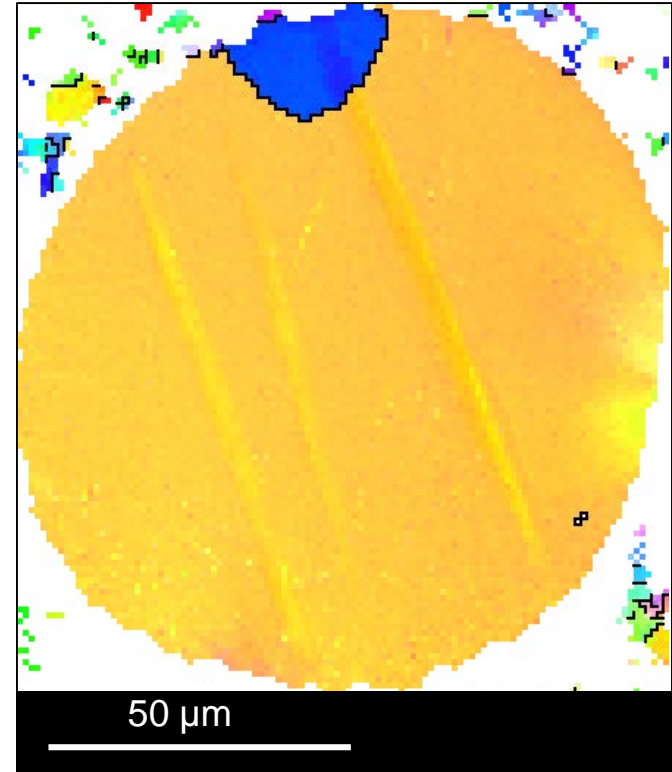
Evidence for the presence of « single crystal » U-Mo particles

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

SEM

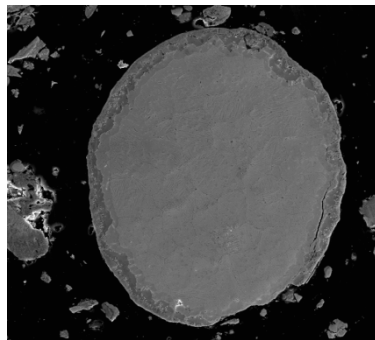
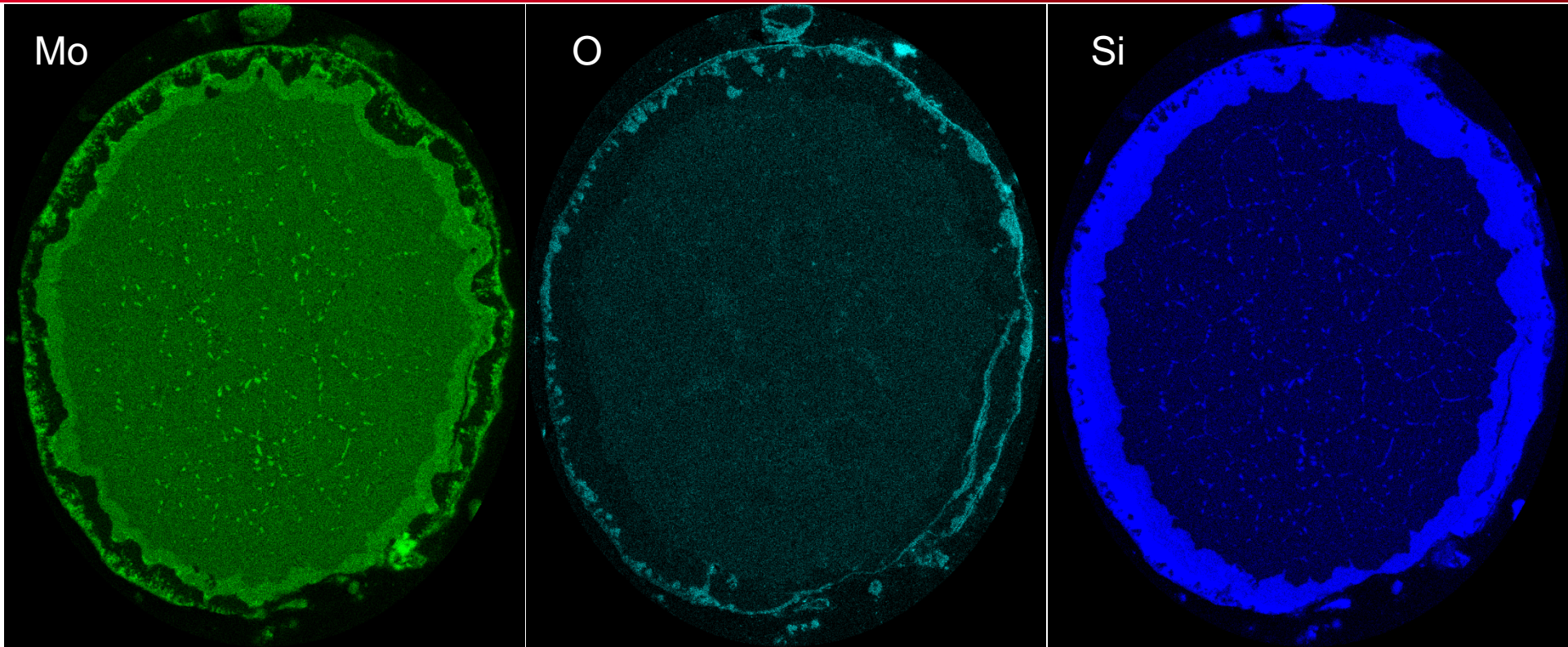


EBSD



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

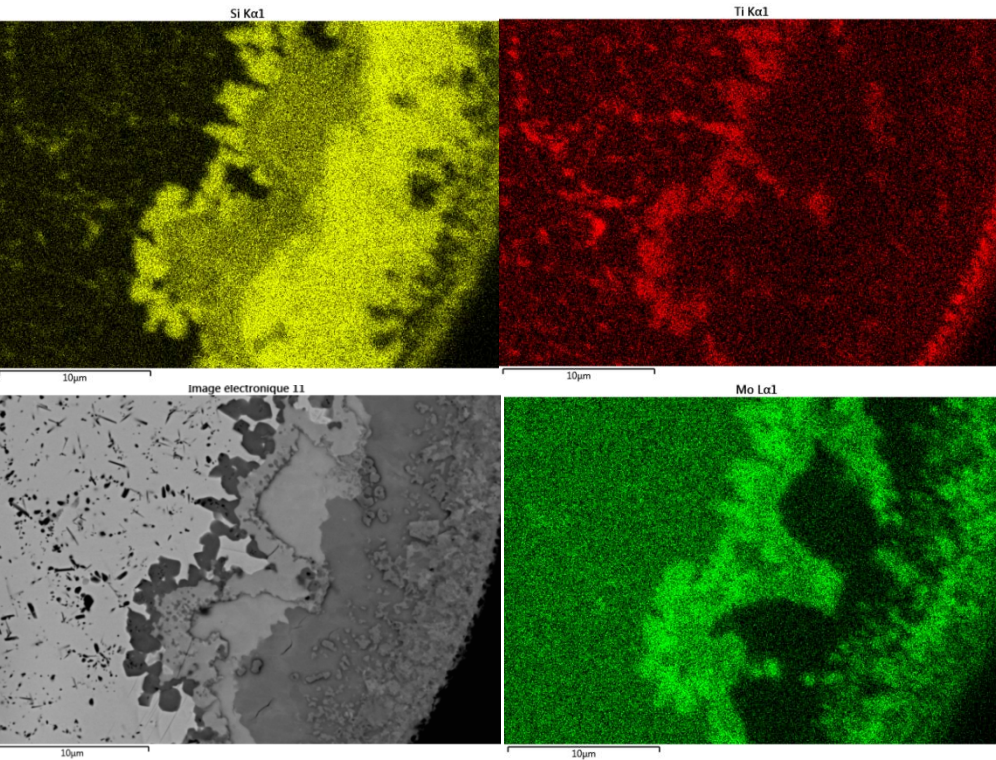
PRECIPITATION AS A RESULT OF THE POWDER ANNEALING



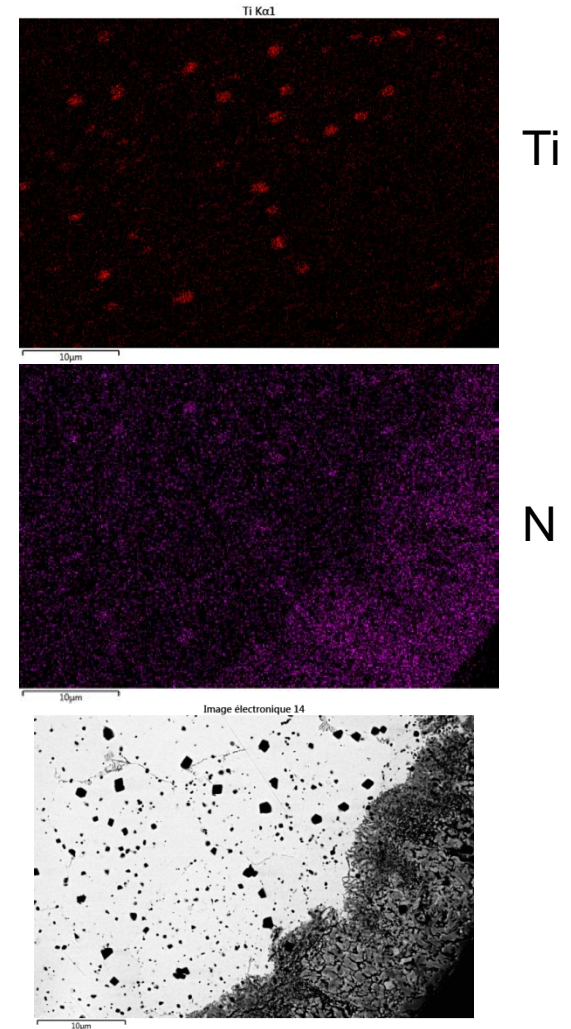
In U-Mo (Si) particles, intergranular Mo-Si rich precipitates can be observed

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

U-Mo-Ti(Si)
(1000°C 1h)



U-Mo-Ti (N)
(1000°C 6h)

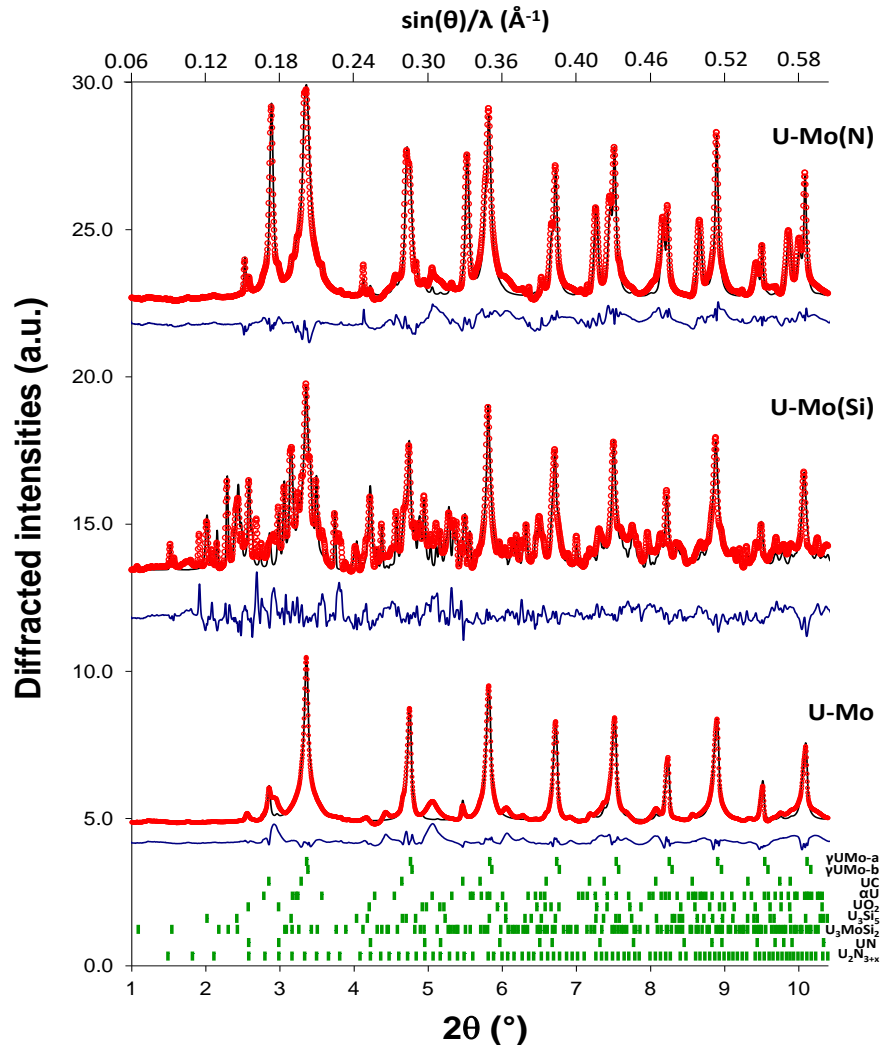


Precipitation of Ti after thermal treatments :

- 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 γU-Mo lattice constants in the as-atomised case only
- Additional tetragonal superlattice
- Quantification of impurities:
U(C,O)
UO₂

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 ₄ N ₇	USi _{1.88}	U ₃ Si ₂	U ₃ Si ₅	U ₃ MoSi 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

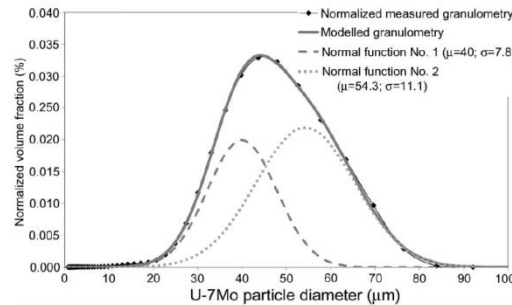
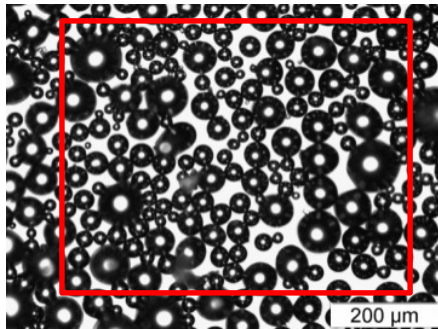
Conclusion :

- No destabilization of the γ U-Mo phase (cooling rate high enough)
- Very high concentration of UN phase in U-Mo(N) (not consistent with 2-3 μ 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%

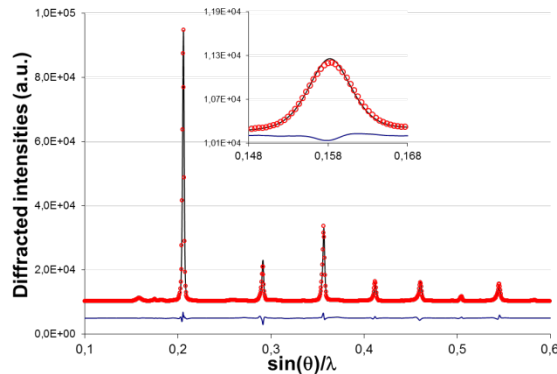
MEASUREMENTS OF THE AVERAGE COATING THICKNESS AT A MACROSCOPIC SCALE

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_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)

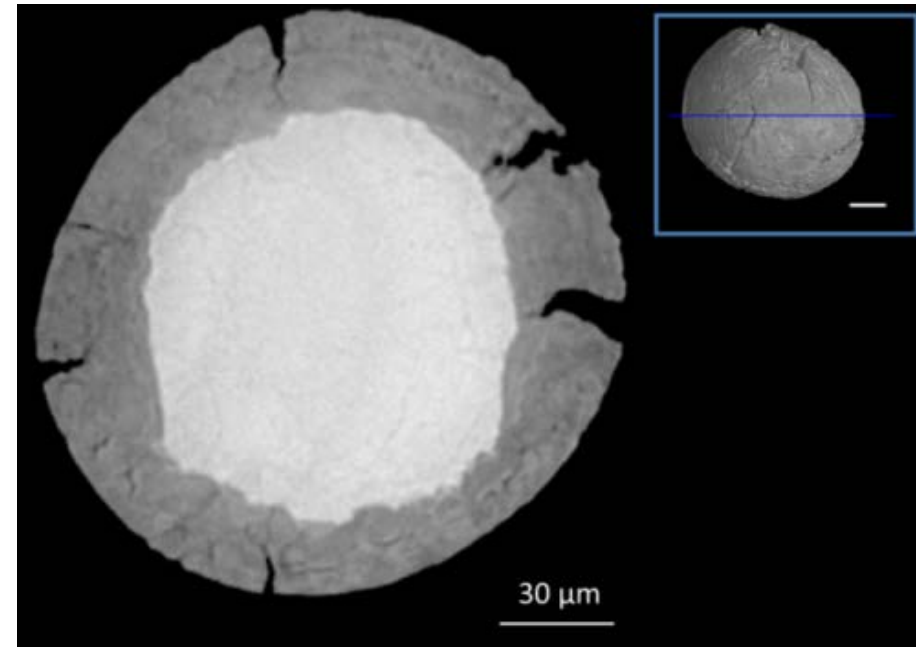
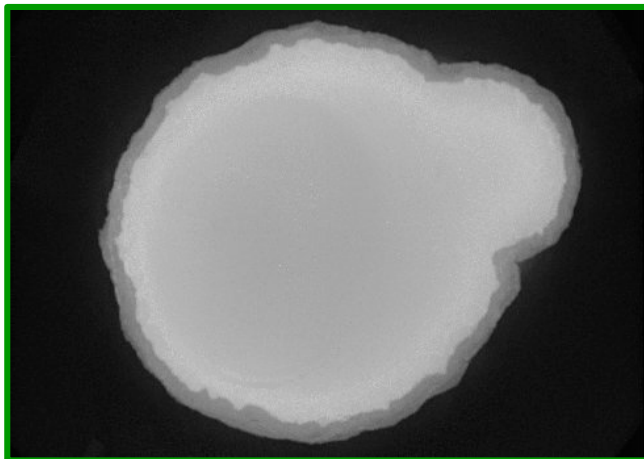
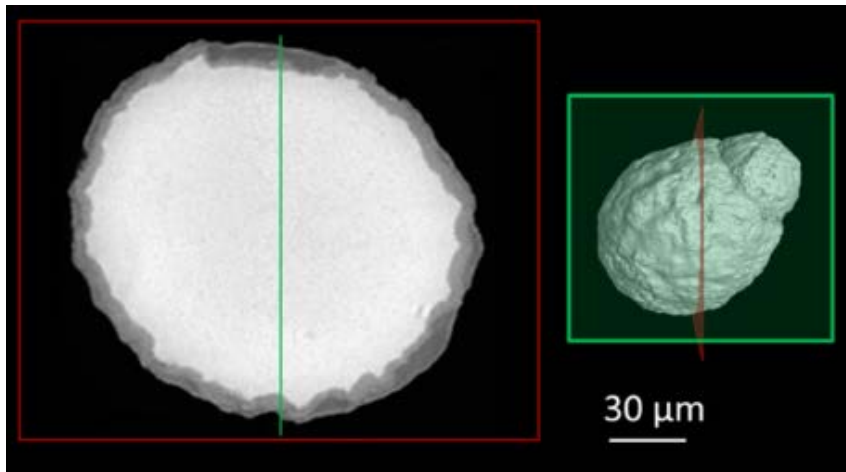
T. Zweifel *et al.*, *J. Nucl. Mater.* (2013). **442**, 124-132.

The UMo(N) case

Phases from the coating represent more than 37 wt% of the material which is not 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

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

ID19@ESRF
Coll. A. Bonnin

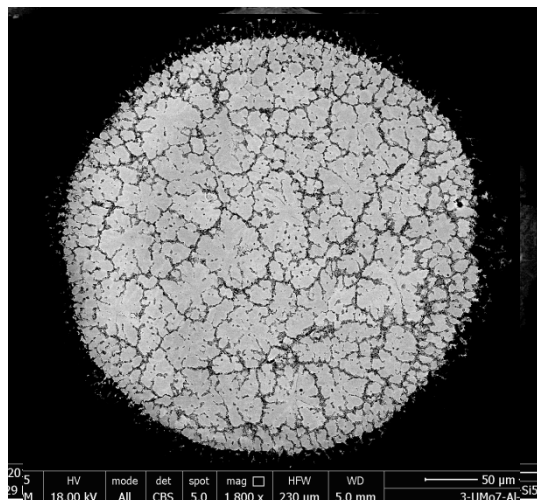


μ-CT helps evidencing:

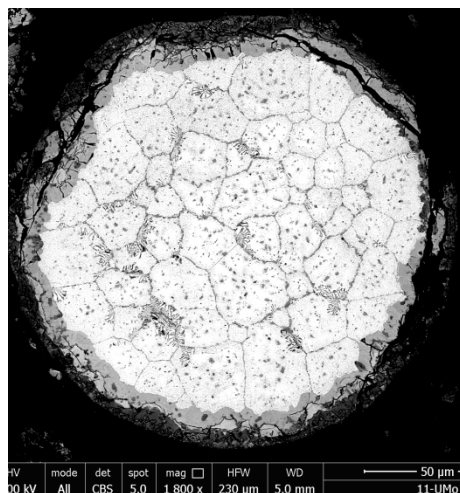
- The good quality of the coating even around particles with non-spherical shapes
- cracks that can not be due to sample preparation contrary to SEM for example.

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

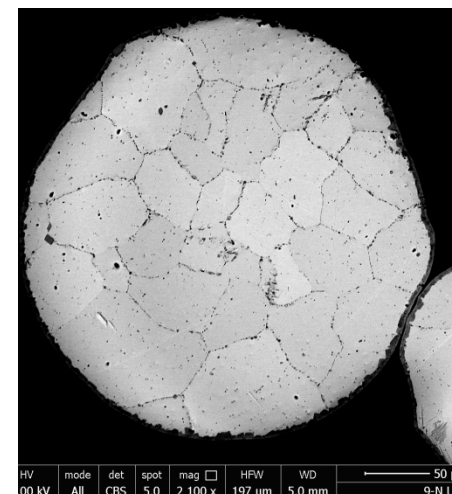
U-Mo(Si)/Al, Si5



U-Mo(Si)/Al
(1000°C 1h)



U-Mo(N)/Al
(1000°C 6h)



SEM examinations:

much higher destabilization of the γ 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 (μm)	<6	15	17
Grain shape	dendritic	Sharpe edges	<ul style="list-style-type: none"> • Sharpe edges • Some « single crystal particles »
Consequences of the coating	---	<ul style="list-style-type: none"> • 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

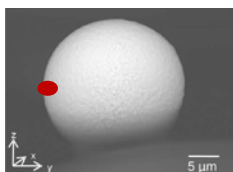
A wide range of cutting edge measurements have been performed to investigate both the coating and the microstructure of U-Mo particles

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Consequences of the coating	---	<ul style="list-style-type: none"> 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

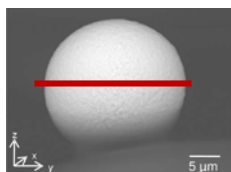
3D MULTI SCALE ANALYSIS OF COATINGS USING SYNCHROTRON RADIATIONS

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

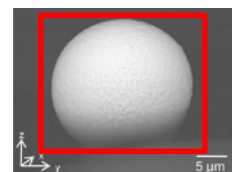
Development of a non destructive approach for coating layers and their evolution at the different steps of the manufacturing process



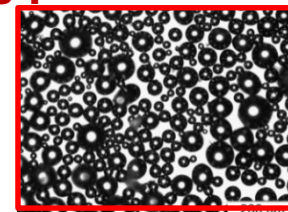
0.1 μm



0.1 μm



20-120 μm



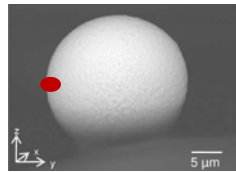
$\sim \text{cm}^2$

X-ray beam size



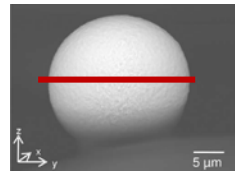
	Nano-XRD	Nano XRD-CT	Far field 3D-XRD	HE-XRD
Crystallographic composition:	×	×	×	×
Thickness:	×	×	×	×
Other coating characteristics (Density, shape, coating/core interface)				HE- μCT ×

As-atomised U-Mo particle microstructure



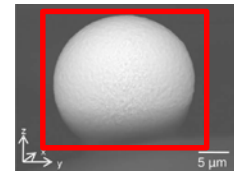
0.1 μm

Nano-
XRD



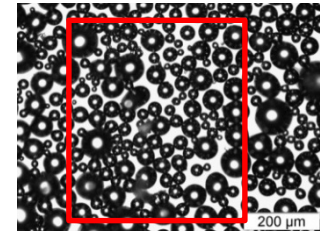
0.1 μm

Nano
XRD-CT



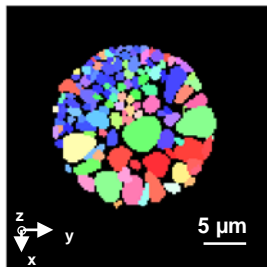
20-120 μm

Far field 3D-
XRD

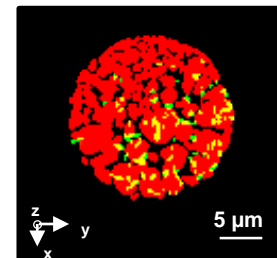


~ cm²

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 γ U-Mo lattice constants
- Additional tetragonal superlattice
- Quantification of impurities:
 $\text{U(C,O)} = 1 \text{ wt.}\%$
 $\text{UO}_2 = 0.3 \text{ wt.}\%$



THANK YOU FOR YOUR ATTENTION