The Abdus Salam International Centre for Theoretical Physics

2359-30

Joint ICTP-IAEA Workshop on Physics of Radiation Effect and its Simulation for Non-Metallic Condensed Matter

13 - 24 August 2012

Current R&D activities on ceramic fuel

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Current R&D activities on ceramic fuel

Thierry Wiss

The European Commission's in-house science service

www.jrc.ec.europa.eu

Serving society
Stimulating innovation
Supporting legislation

Commission européenne

The JRC - ITU

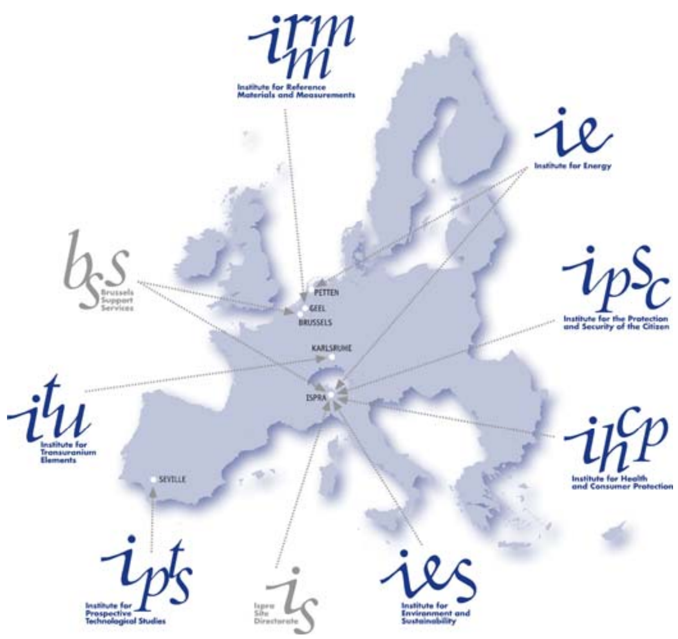
7 Institutes in 5 Member States **(4 with nuclear activities)**

IRMM - *Geel, Belgium*
Institute for Reference Materials and Measurements

ITU - *Karlsruhe, Germany*
Institute for Transuranium Elements

IE - *Petten, The Netherlands – Ispra, Italy*
Institute for Energy

IPSC - *Ispra, Italy*
Institute for the Protection and Security of the Citizen



Governance:

Board of Governors (Member States)

EU parliament (Framework Programme, budget)

~ 2750 staff
~ 330 M€/y budget (+ 40 M€/y competitive income)

Joint Research Centre

Criteria for fuel materials

- **Low neutron capture cross section of non-fissile elements**
- **High fissile density**
- **No chemical reaction with cladding or coolant**
- **Favourable physical properties, especially thermal conductivity and melting point (together give the margin to melting)**
- **High mechanical stability (isotropic expansion, stable against radiation)**
- **High thermal stability (no phase transitions, no dissociation)**
- **High radiation resistance**

Potential fuel materials

e.g. UO_2

Fuel composition
Metal
Oxide
Nitride
Carbide
Fluoride (salt)

Fuel form
Single phase
Solid solution
Composite

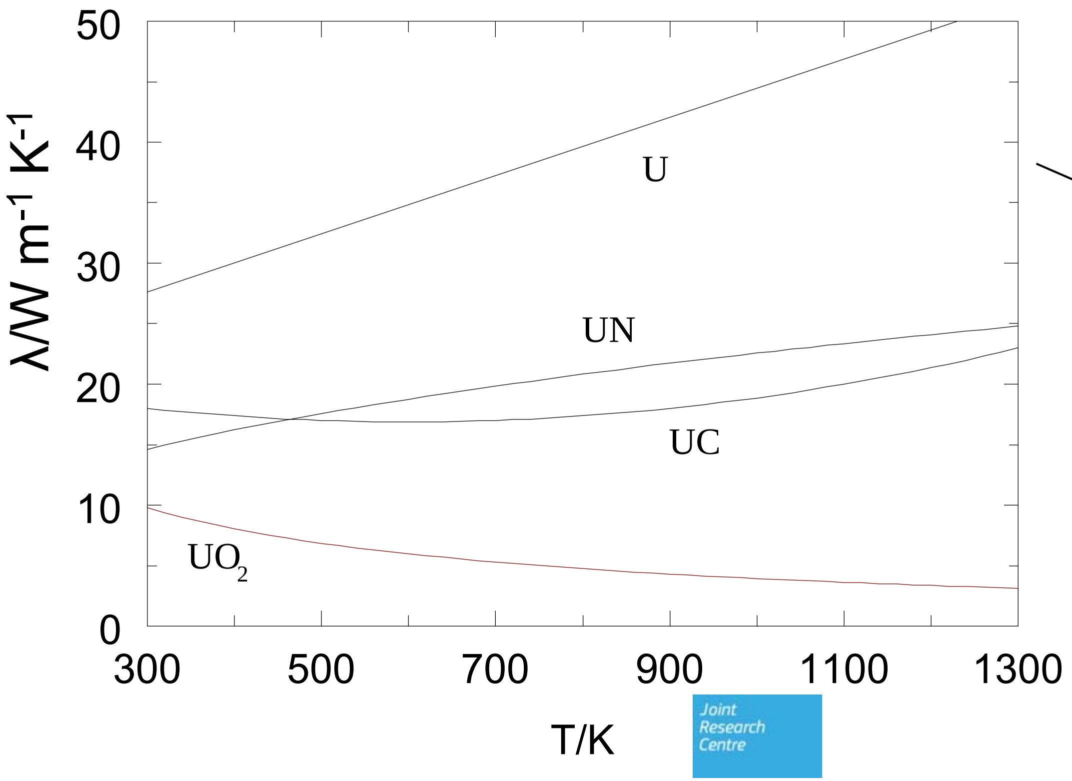
Fuel packing
Pellet
Particle
Liquid

e.g. $(U,Pu)O_2$

e.g. $Mo+UO_2$

Properties of U compounds

	Melting point (K)	Density (g cm^{-3})	U-density (g cm^{-3})
U	1308	19.05	19.05
UO_2	3073	10.95	9.6
UC	2798	13.63	12.97
UN	3123	14.32	13.53



Margin to melting

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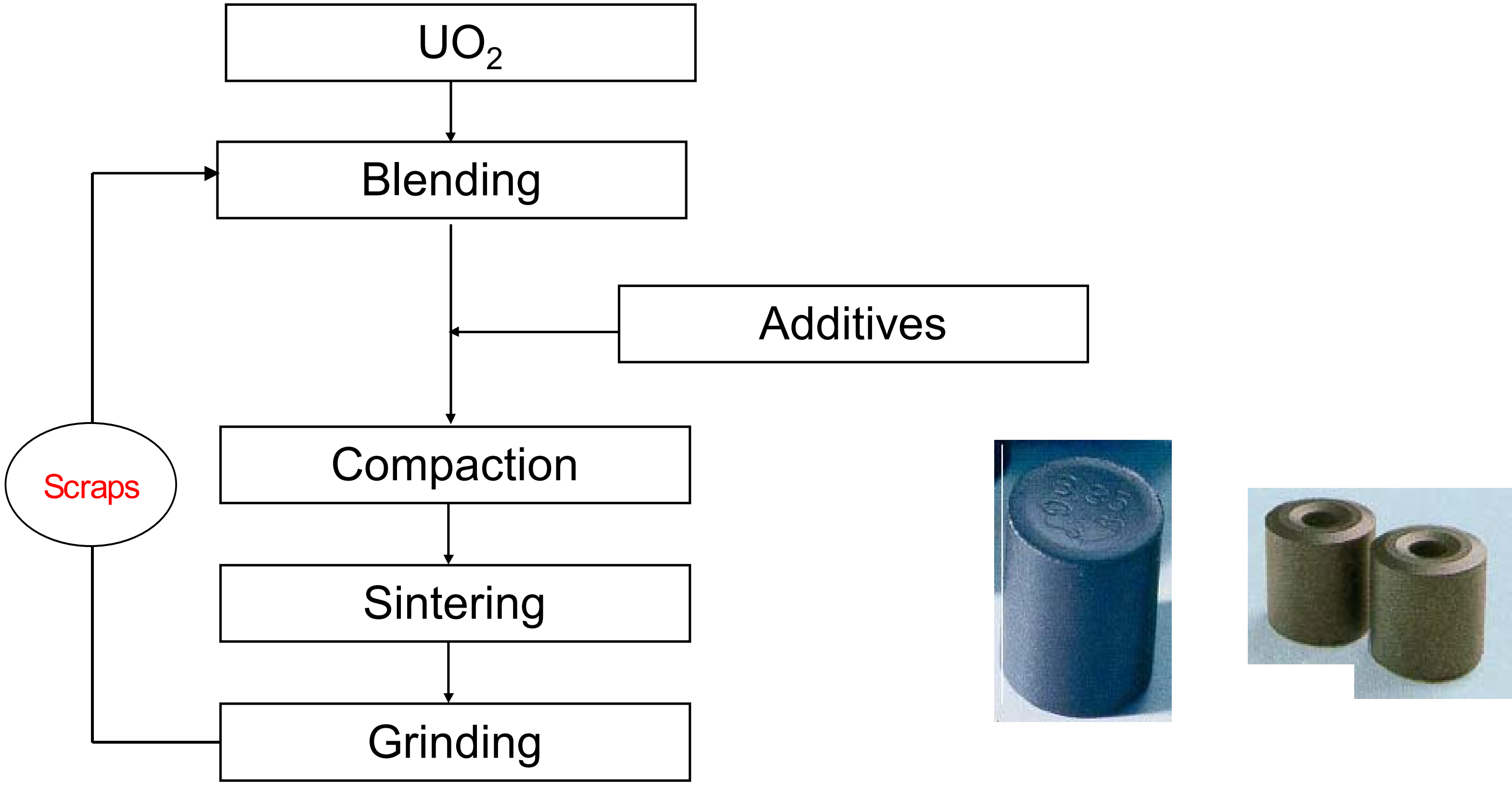
Fuel materials used in reactors

Light-water	PWR, BWR	UO_2
Heavy-water	CANDU	UO_2
Graphite-moderated	AGR, RBMK	UO_2
High-temperature gas cooled	HTR	UO_2, (ThO_2, UC)
Sodium-cooled	SPX, Monju	$(U,Pu)O_2$
	EBR-II	(U,Pu) (U,Pu,Zr)
	PBTR	(U,Pu)C
Molten salt	MSR	$LiF/BeF_2/ThF_4/UF_4$

Fabrication of UO_2 pellets (compacts)



LWR AGR

Content

Methodology (samples, Knudsen Cell, SEM/TEM, Cp)

Release of FGs and microstructure evolution f(BU, T)

- I – UO_2 irradiated at 96 GWd/t_U
- II – MOX irradiated at 44.5 GWd/t_M
- III – UO_2 irradiated at local BU 220 GWd/t_M
- IV - nitride fuels

Basic mechanisms of damage formation

- V – $(U_{0.9},{}^{238}Pu_{0.1})O_2$

Conclusions

Context

The knowledge of the behaviour of the nuclear fuels at high burnup

- **Fission gas release is a key issue affecting in-pile safety and performance of nuclear fuel.**
- **Formation of the High Burnup Structure can affect the stability of the fuel.**
- **Risk assessment on fuel operation in abnormal conditions (temperature excursion)**
- **Source term for spent fuel in accidental/storage condition.**

HBS

HBS (or RIM) structure is formed at high local burnup and low T_{irr}. It is characterized by Xe depletion from the matrix of newly formed small grains, coarsened fission gas pores of micrometric size, sub-division of the initial grains from typically 10 µm to 0.15-0.30 µm, and evolves to an "ultimate" microstructure at very high burnup.

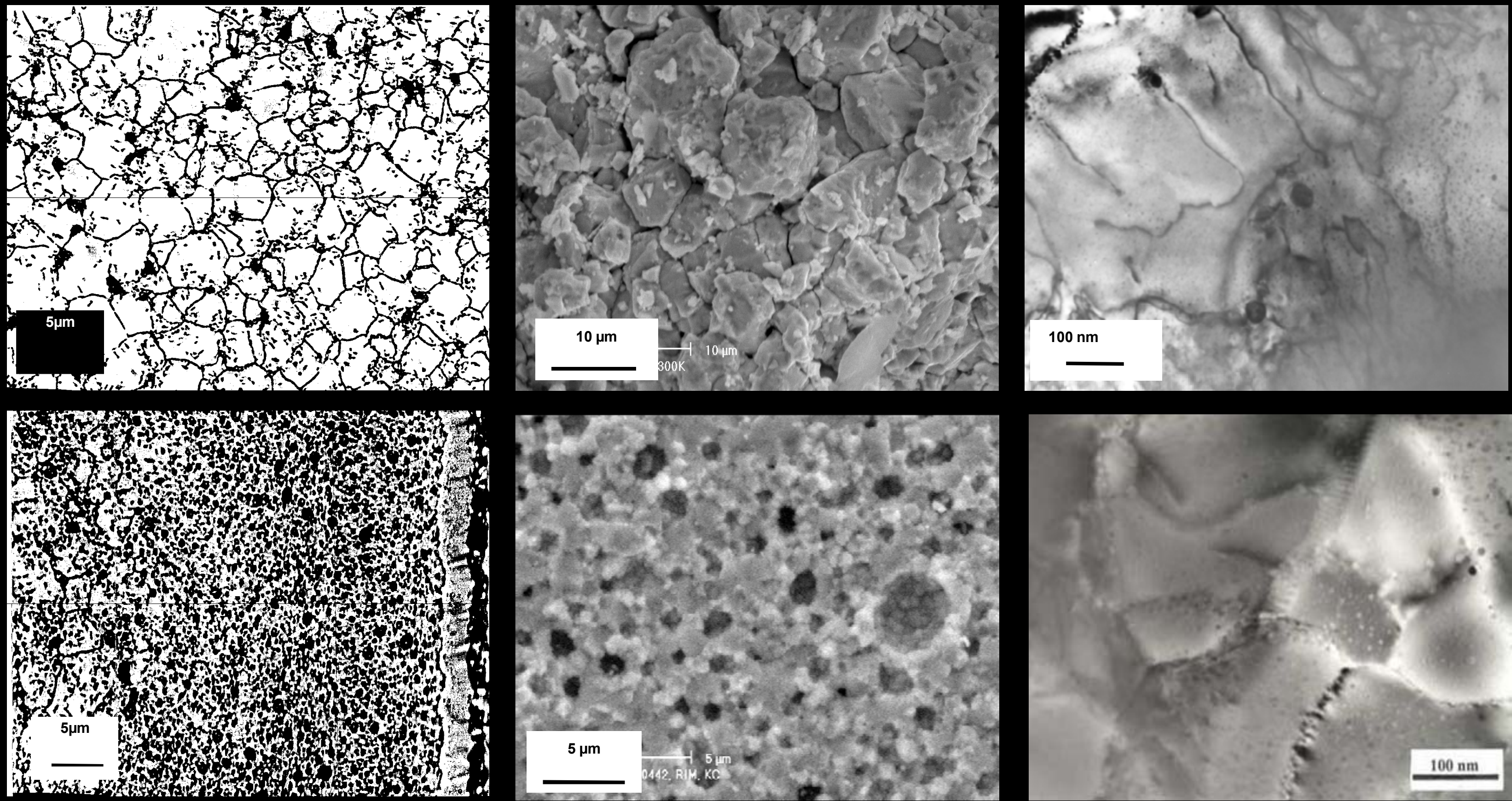
Although the development of the HBS is well documented (burn-up threshold, effect on fission gas release, structural changes...), there is currently no model able to properly simulate its formation and extension inwards the fuel pellet.

HBS

Optical | SEM | TEM

Std.

HBS



Methodology

- The SEM were performed on small fragments (fresh, annealed).

- The TEM were performed by crushing small fragments of fuel.

- The Knudsen Cell experiments were performed by selecting (radial position if necessary) small samples of ~ 2-10 mg.

- The relation between structural changes, burn-up, irradiation temperature and fission gases release is determined.

- Single effect studies are performed to assess basic mechanisms.

Samples

I - HBRP samples: consist in small discs of 5 mm Ø and 1mm thick of UO_2 enriched 25 % ^{235}U. These disks were sandwiched between Mo discs and irradiated without mechanical constrain in the gas flow rig, IFA-601, to obtain very homogeneous burnup and temperature profile

II - MIMAS PWR MOX fuel with an average burn-up of 44.5 GWd/tHM.

III - very high burnup UO_2 : The samples were small pieces of 4 and 6 mg chosen at the periphery (1> r/ro > 0.93) of a fuel pellet of cumulative average burn-up of 98 GWd/tHM. The mean local burn-up of these samples is 220 ± 20 GWd/tHM

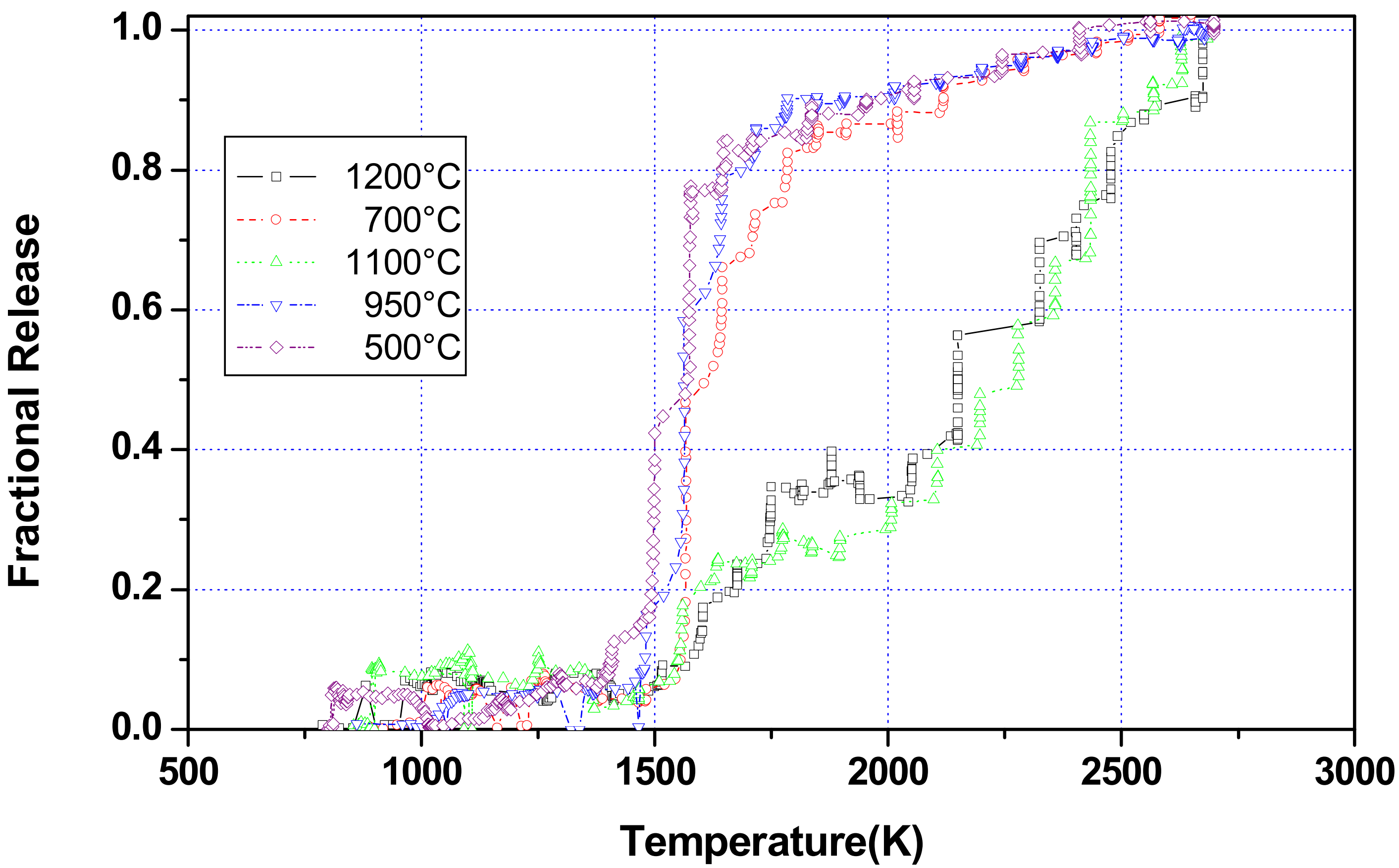
IV – the nitride samples are produced in nitrogen boxes

V - 10 wt% (labeled UO2-10) of an oxide constituted mainly of ^{238}Pu, A sol-gel technique was used to ensure an intimate mixing of the α-emitters with the UO_2 matrix.

I - HBRP 96 GWD/tU

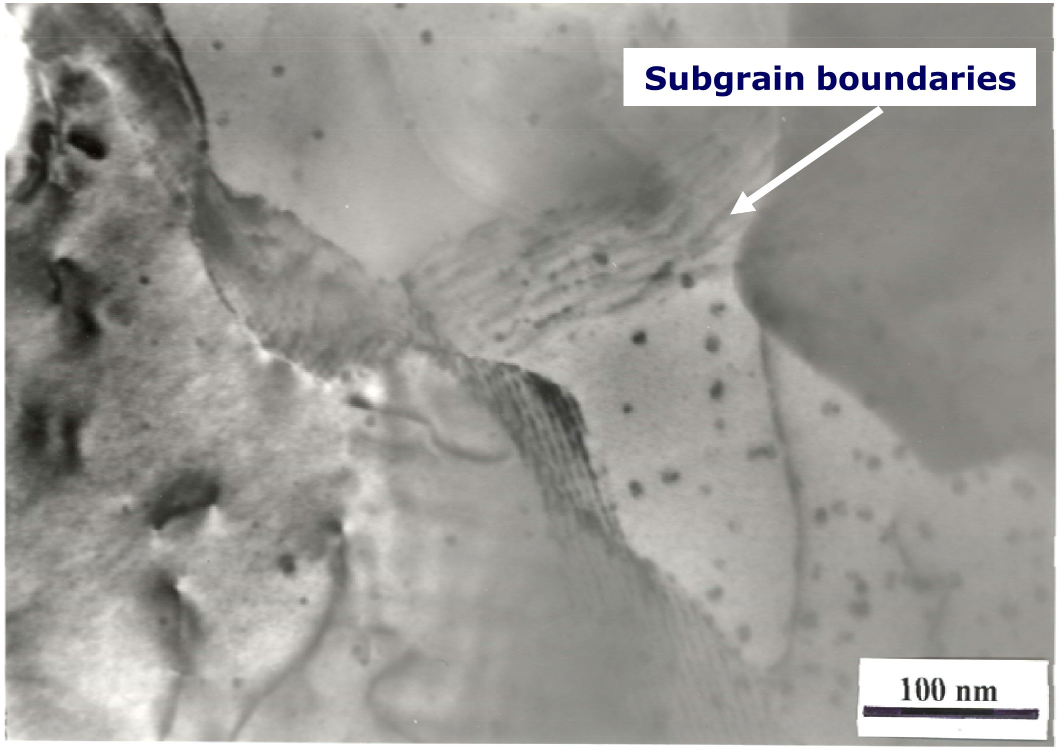
I - Kr release (HBRP)

BU = 90 - 96 GWj/t_U



I - TEM (HBRP)

BU = 96 GWj/t_U T = 460 ° C



Full restructuring Small bubbles + FPs precipitates

Kinoshita, M., Sonoda, T., Kitajima, S., Sasahara, A., Kameyama, T., Matsumura, T., Kolstad, E., Rondinella, V.V., Ronchi, C., Hiernaut, J.-P., Wiss, T., Kinnart, F., Ejton, J., Papaioannou, D., Matzke, Hj., High Burnup Rim Project: (III) properties of rim-structured fuel, 2004, Proceedings of the 2004 International Meeting on LWR Fuel Performance, Orlando, FL, pp. 207-213

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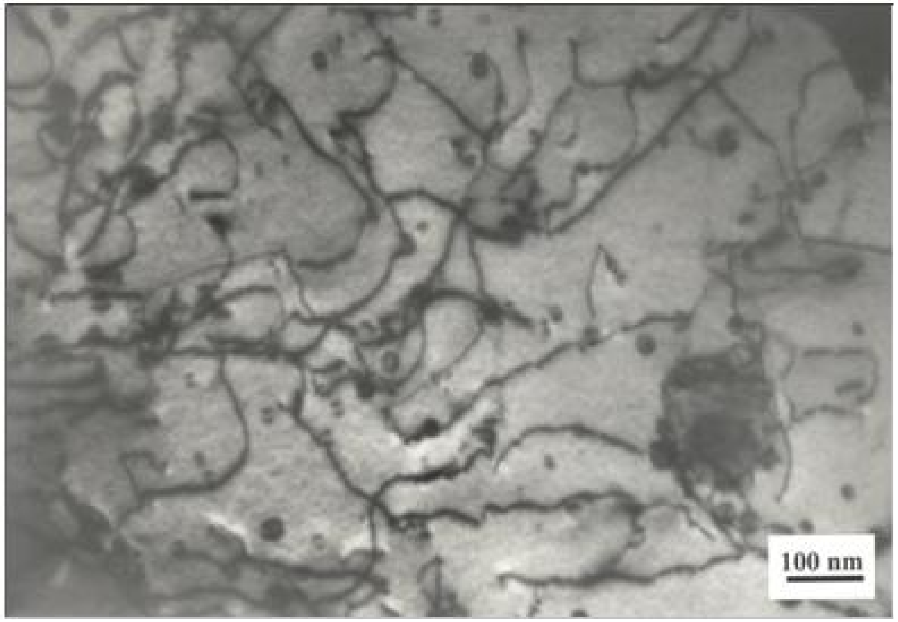
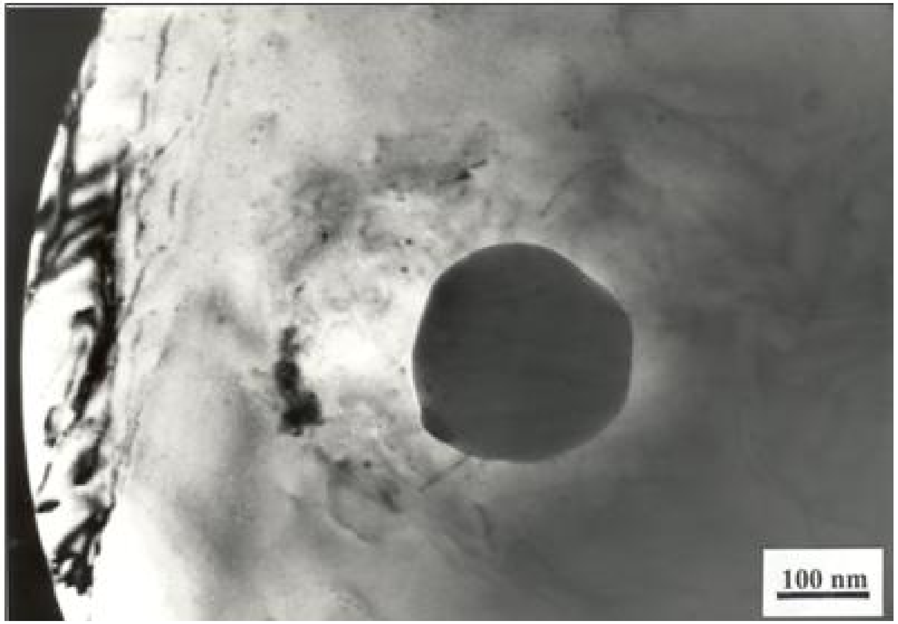
BU = 92 GWj/t_U T = 1220 ° C

I - TEM (HBRP)





No restructuring, large ε particles

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II - MOX

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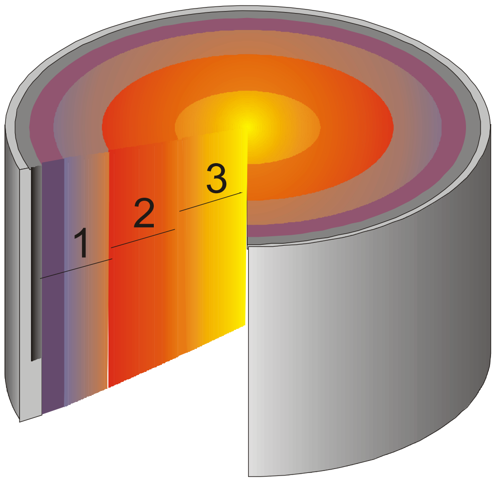
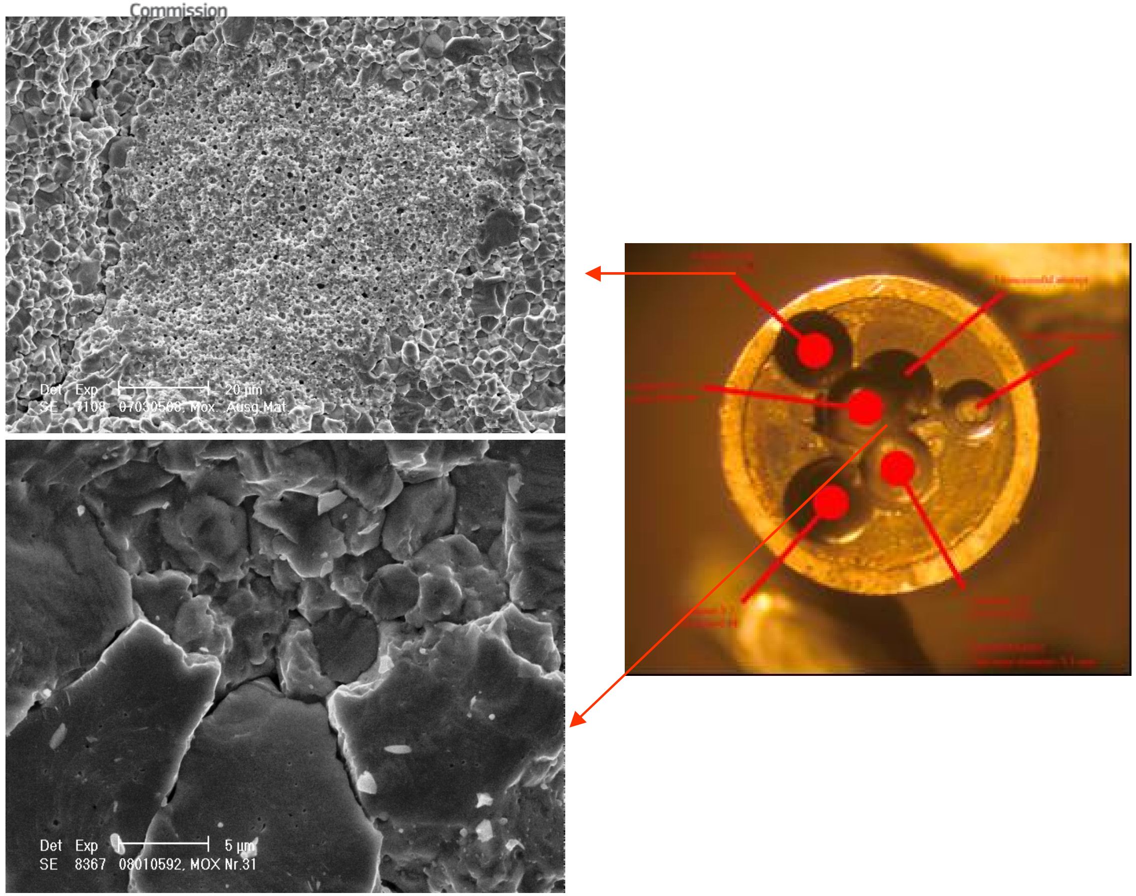
II - MOX



MOX fuel BU 44.5 GWd/tHM



Sample type 1: region close to the cladding:0.89<r/ro<0.64; ($T_{irr.}$ ~ 700 °C)

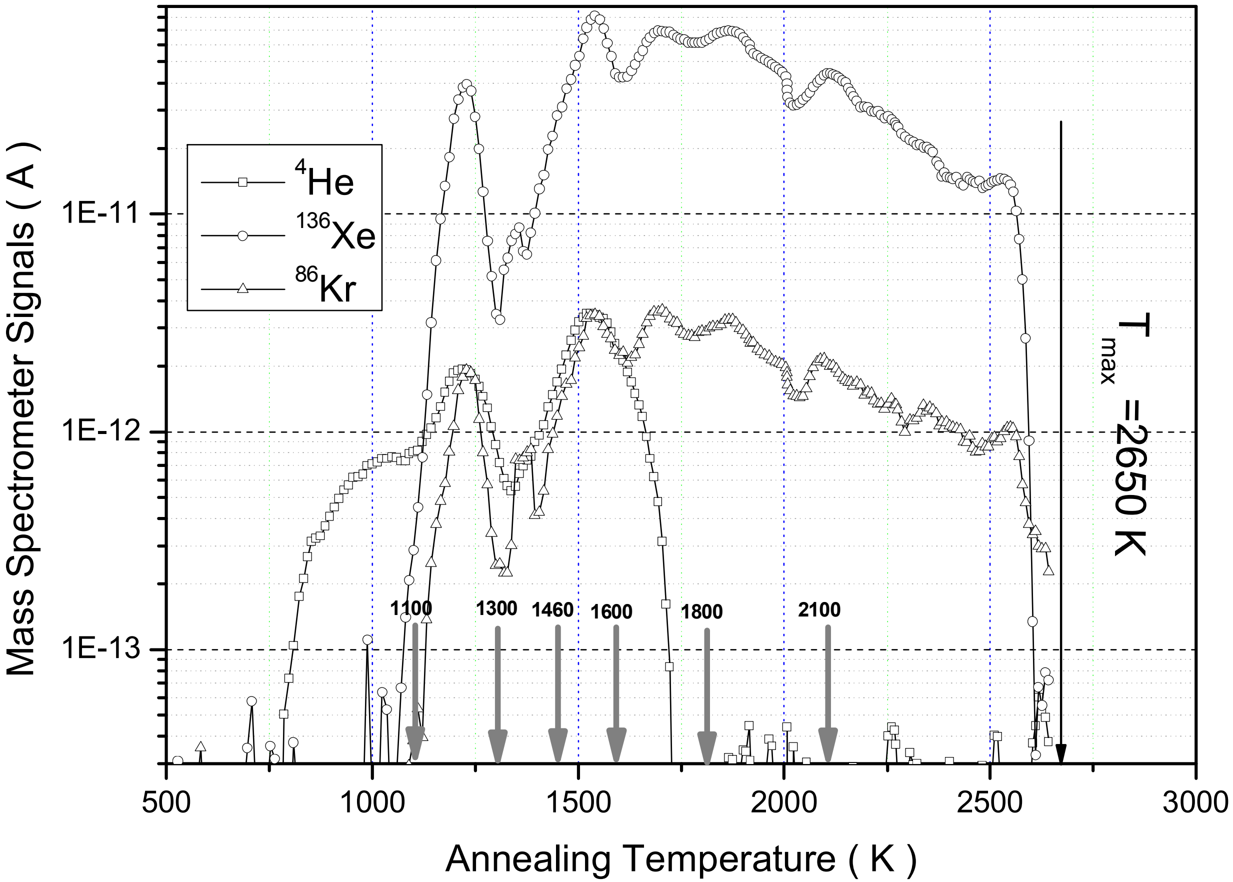
Sample type 2: intermediate region of the pellet: 0.84<r/ro<0.56; ($T_{irr.}$ ~ 800 °C)

Sample type 3 : central region of the pellet: 0.34<r/ro<0.09, ($T_{irr.}$ ~ 1200 °C)

II - Gas-release MOX

MOX (type 1)

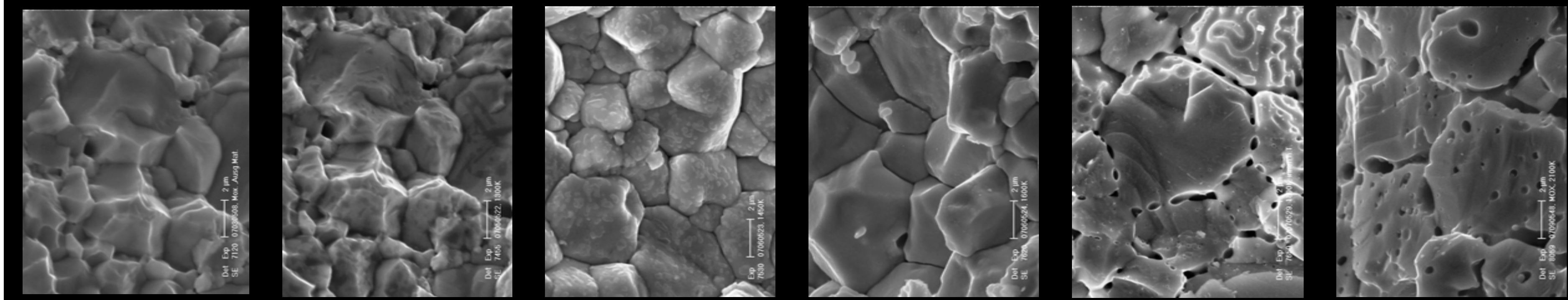
The arrows indicate where SEM was performed



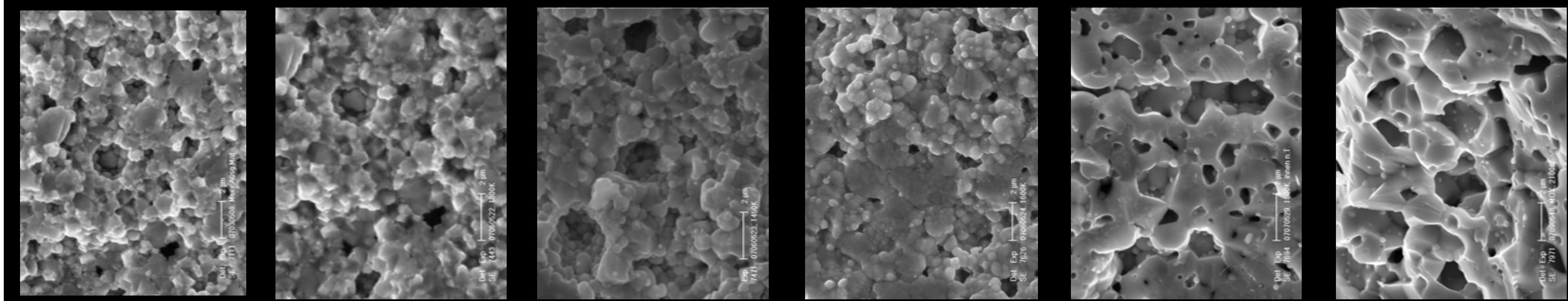
Wiss, T., Hiernaut, J.-P., Colle, J.-Y. Thiele, H., Rondinella, V.V., Konings, R.J.M., Sasahara, A., Sonoda, T, Kitajima, S., Fission Gas Release and Microstructural Features During Thermal Annealing of Irradiated Fuels, Transactions of the American Nuclear Society, Vol. 104, Hollywood, Florida, June 26–30, 2011

II - SEM of MOX **(type 1)**

UO_2 matrix



300 K | 1300 K | 1450 K | 1600 K | 1800 K | 2100 K



Pu-rich area

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III - UO2 very high burn-up

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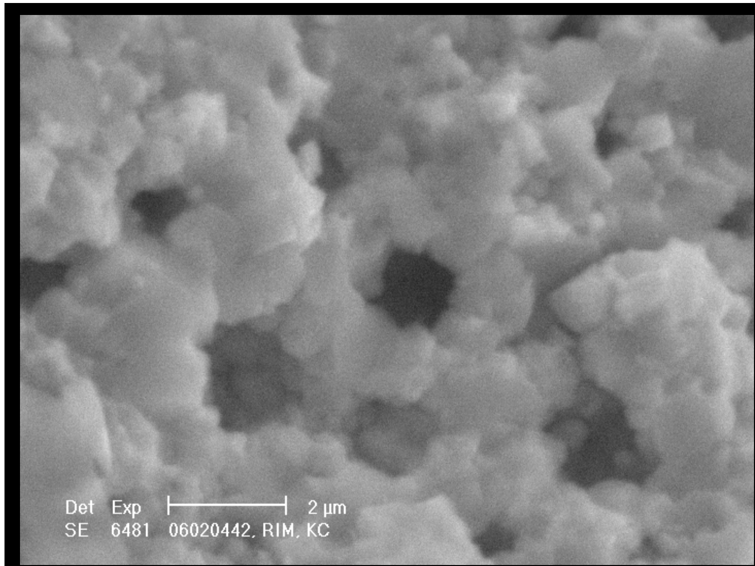
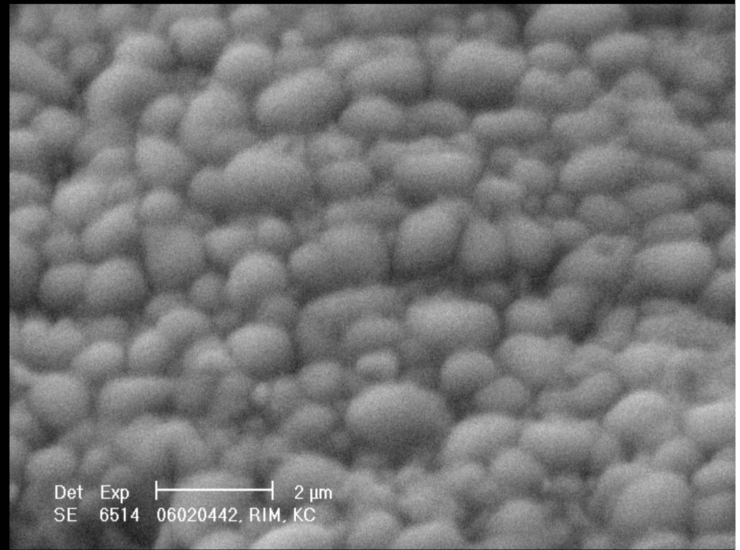
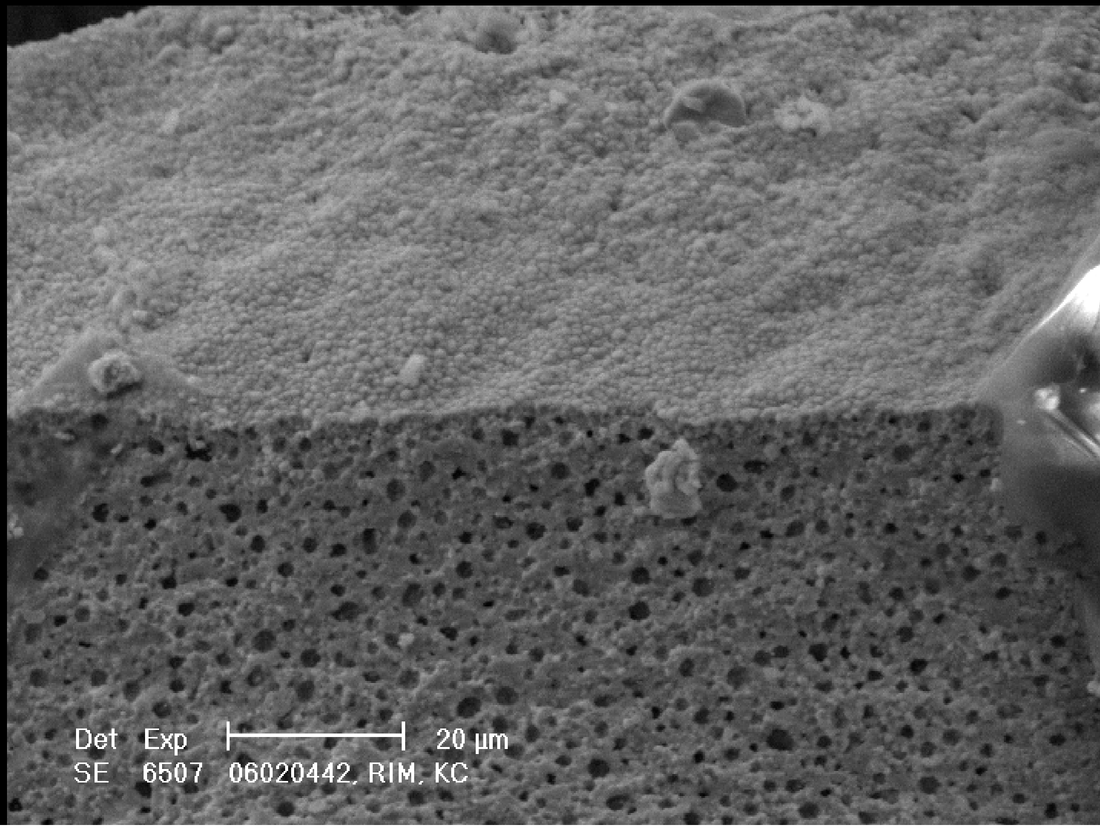
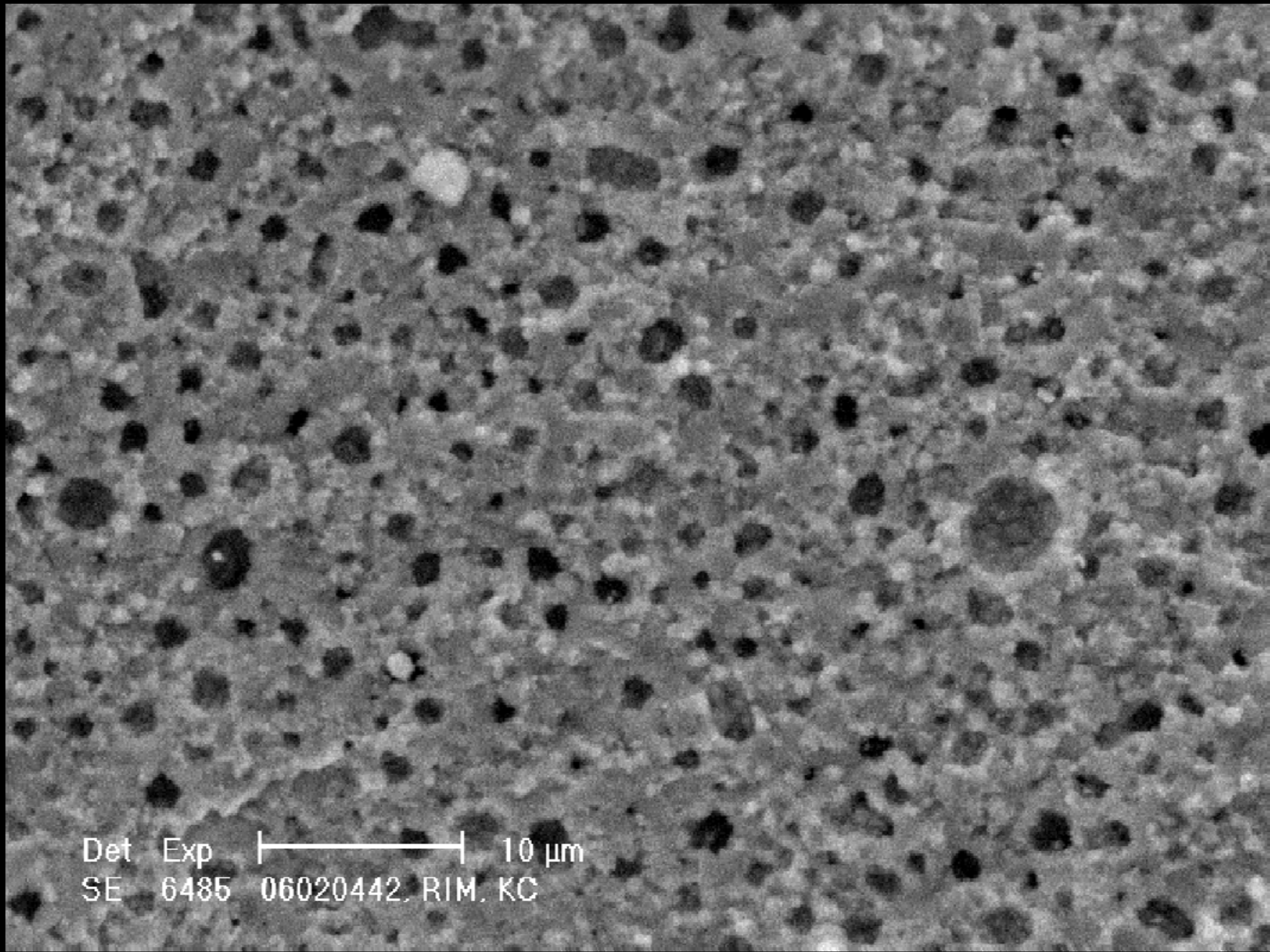


LWR 220 GWd/t As irr.



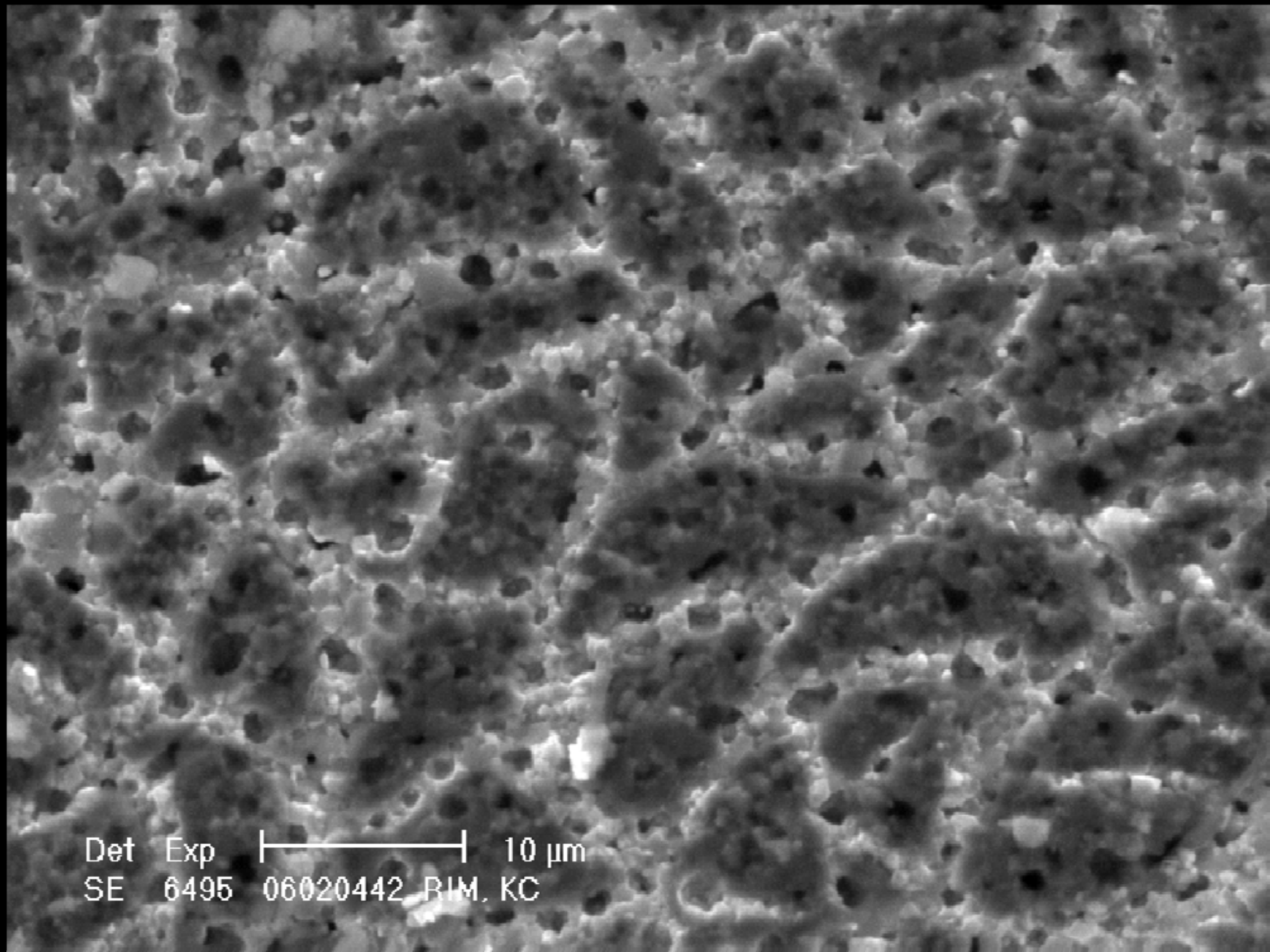


As irr.



Hiernaut, J.-P., Wiss, T., Colle, J.-Y., Thiele, H., Walker, C.T., Goll, W., Konings, R.J.M.,
Fission product release and microstructure changes during laboratory annealing of a very high burn-up fuel specimen,
2008, Journal of Nuclear Materials 377 (2), pp. 313-324

As irr.



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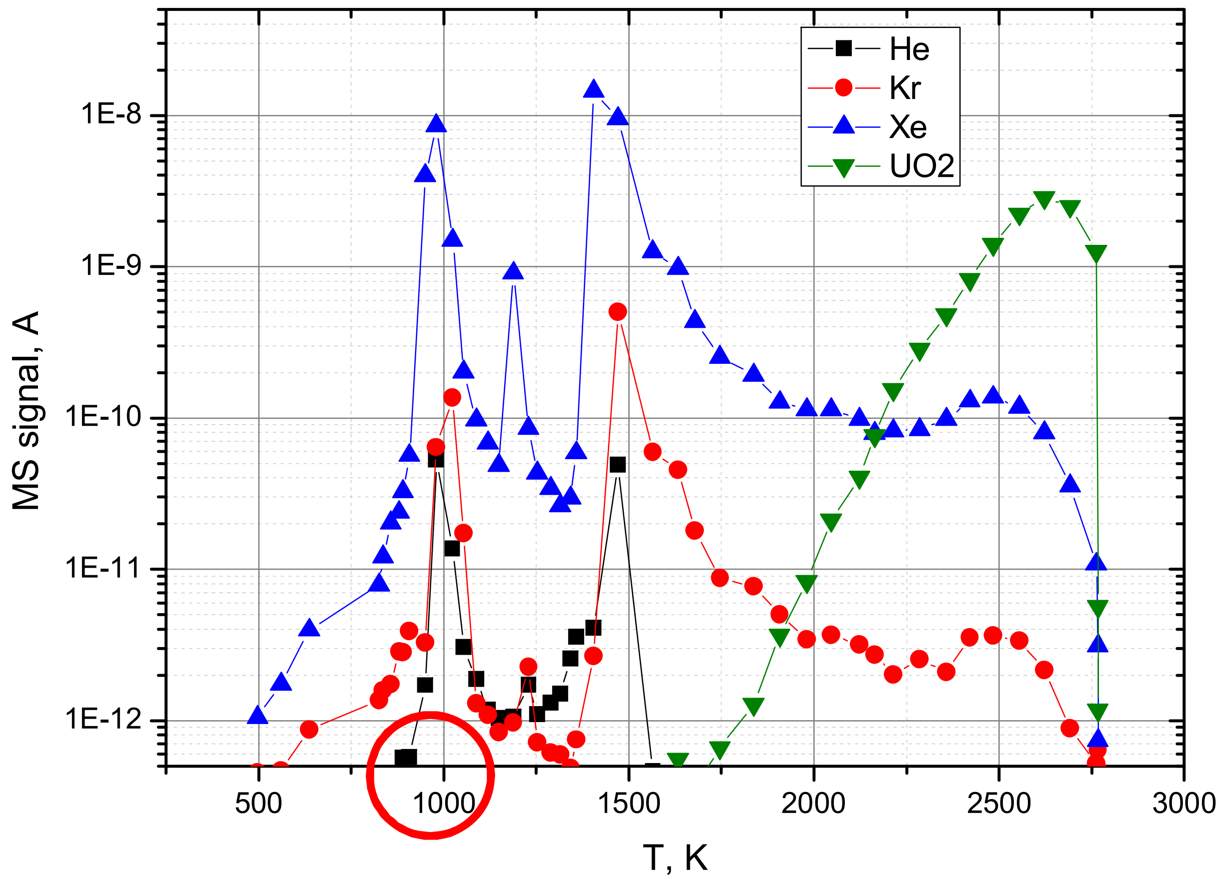
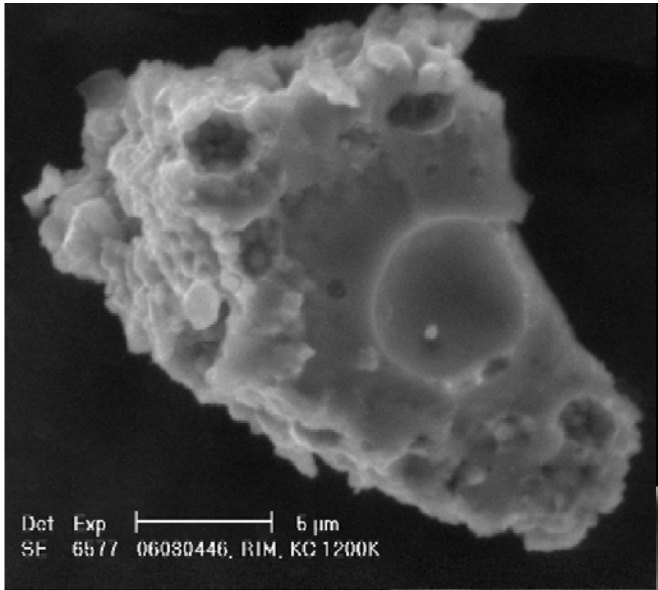
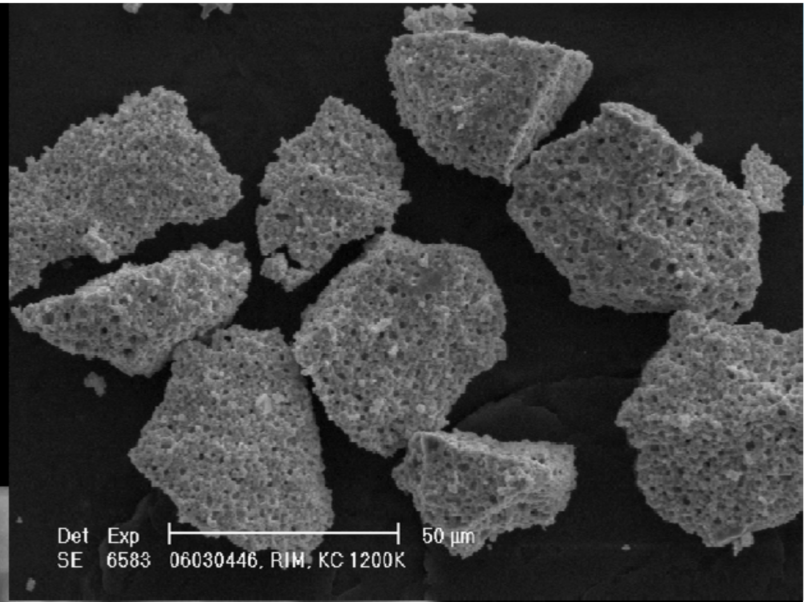
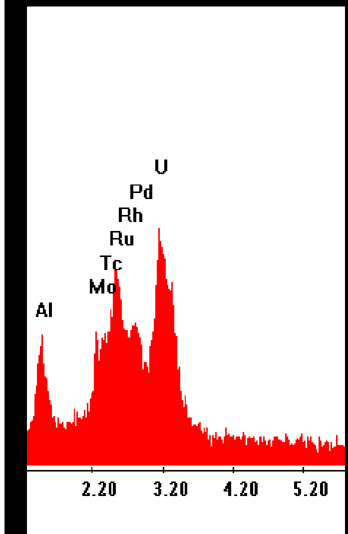
III -Gas release from HBS

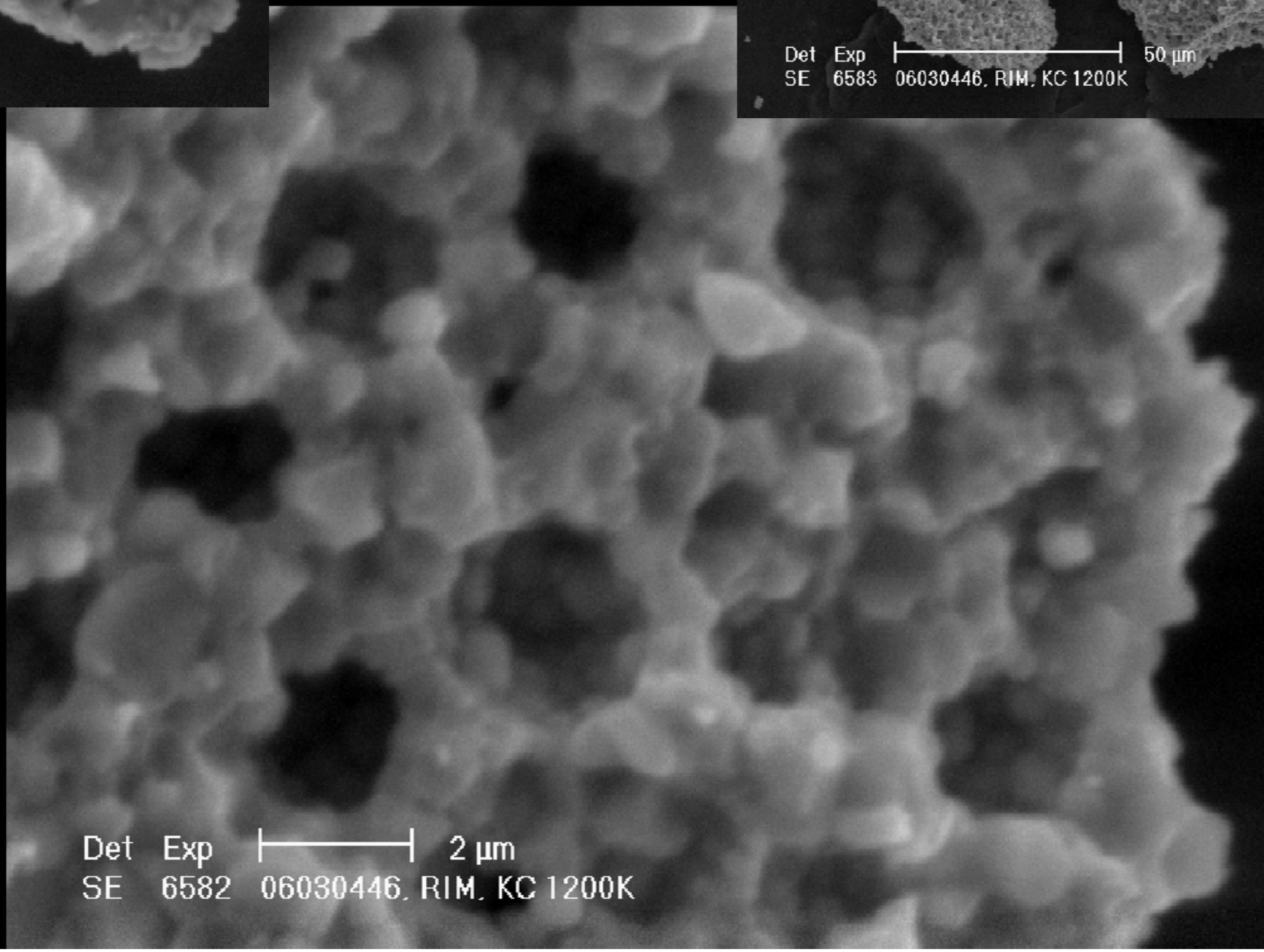



Det Exp 5 µm
SE 6577 06030446, RIM, KC 1200K

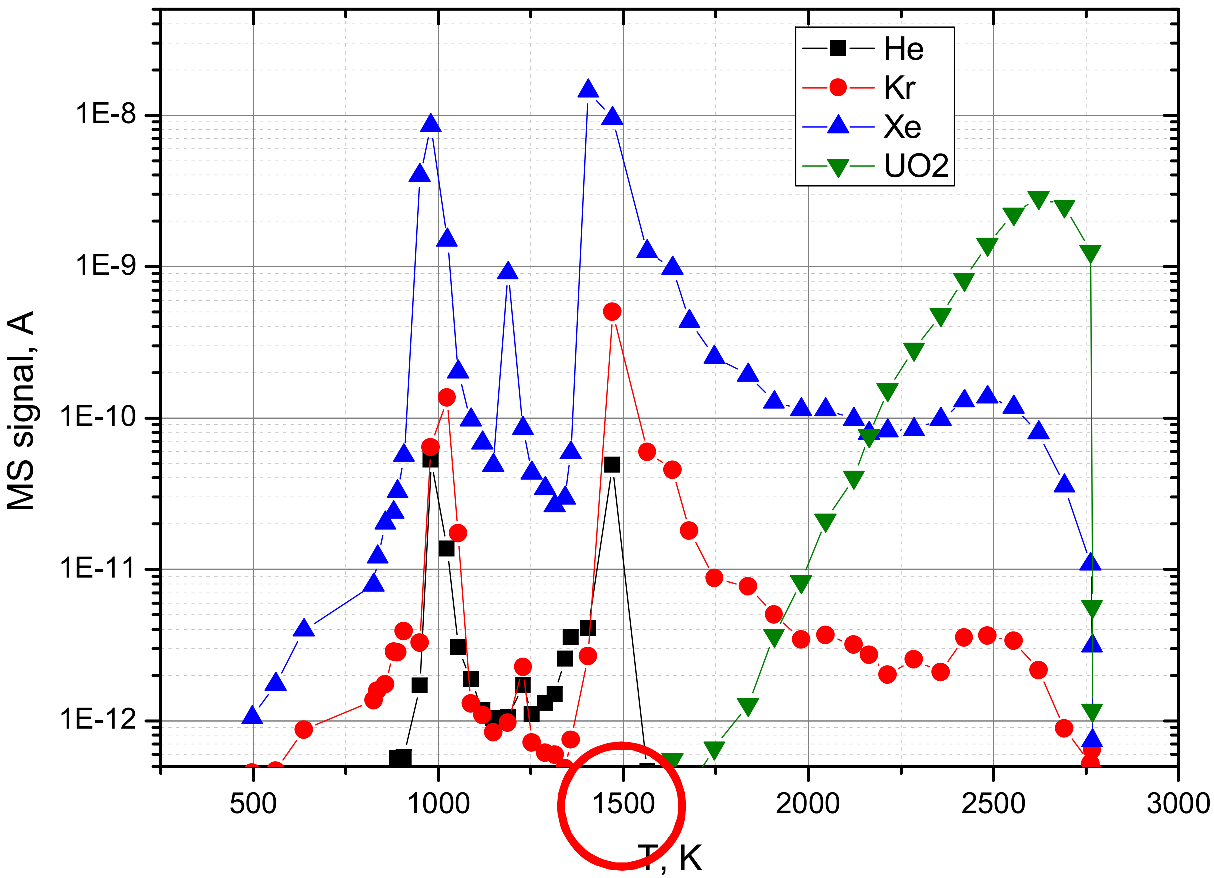
920 K

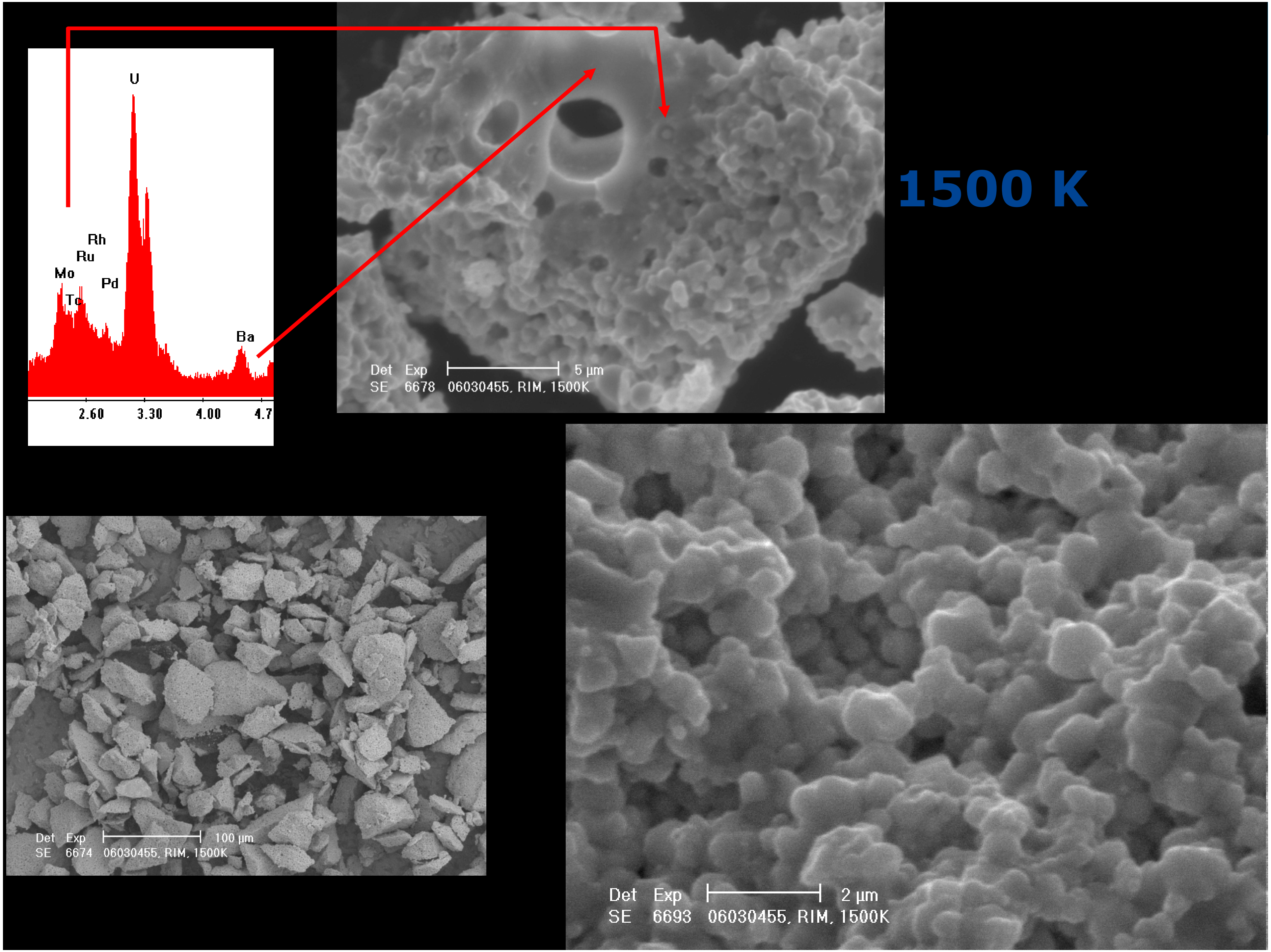

Det Exp 50 µm
SE 6583 06030446, RIM, KC 1200K


U
Pd
Rh
Ru
Tc
Mo
Al
2.20
3.20
4.20
5.20


Det Exp 2 µm
SE 6582 06030446, RIM, KC 1200K

III - Gas release from HBS




U
Rh
Ru
Mo
Pd
Tc
Ba
2.60
3.30
4.00
4.7
Det Exp 5 µm
SE 6678 06030455, RIM, 1500K
1500 K
Det Exp 100 µm
SE 6674 06030455, RIM, 1500K
Det Exp 2 µm
SE 6693 06030455, RIM, 1500K

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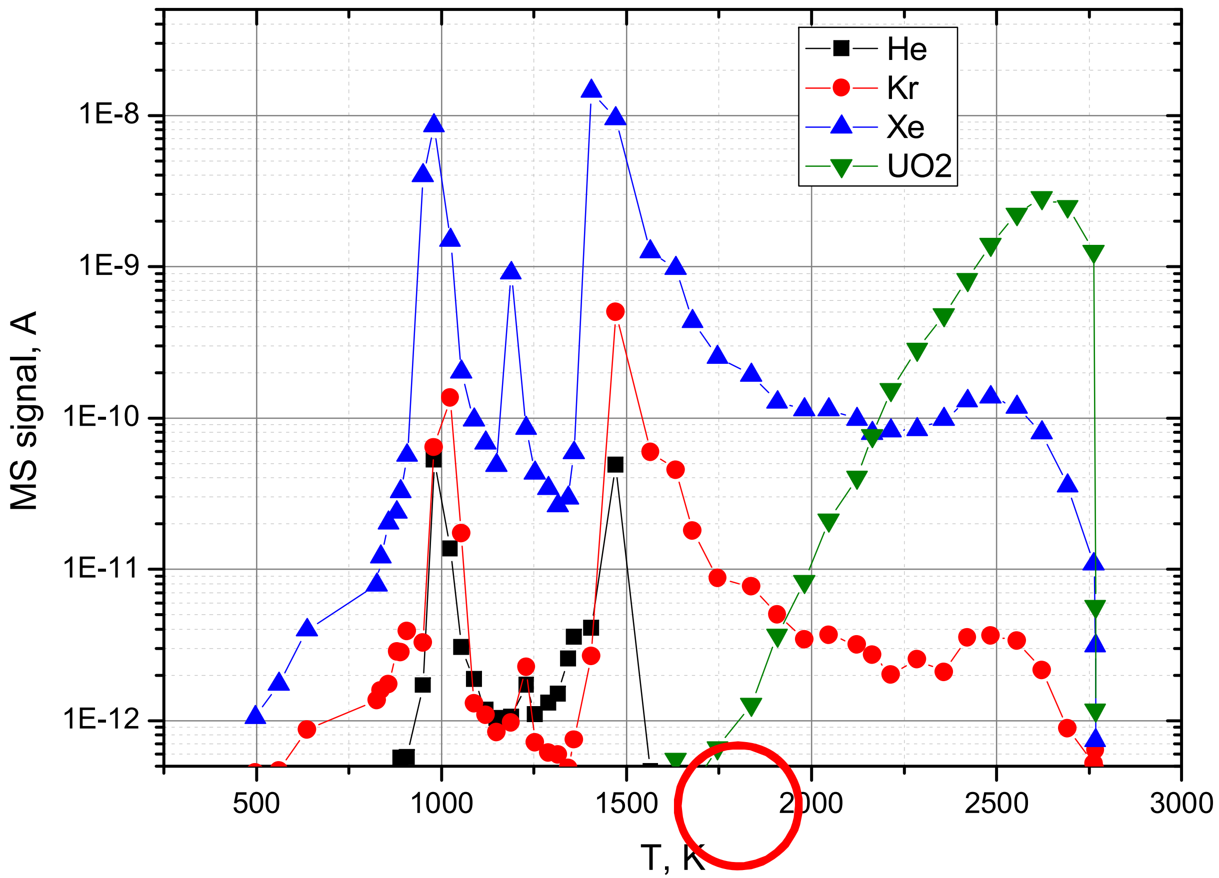
III - Gas release from HBS



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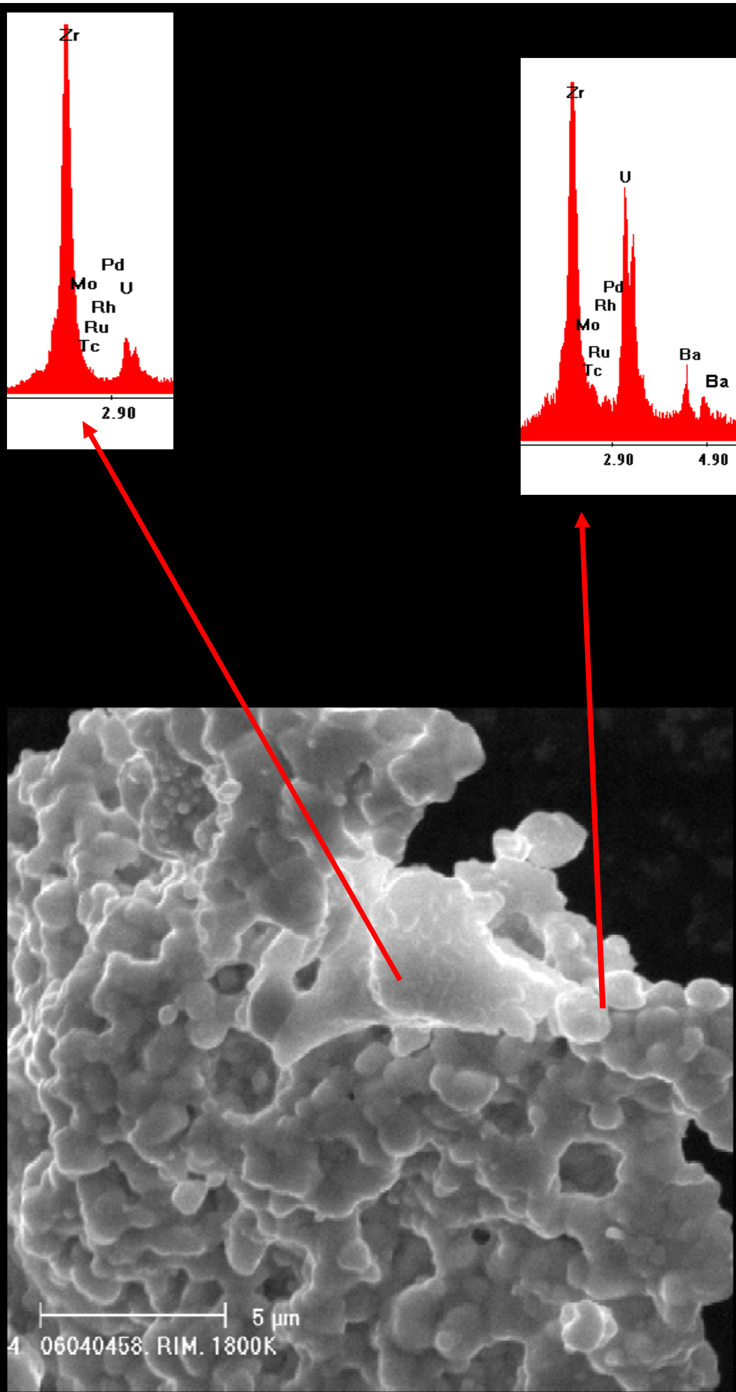
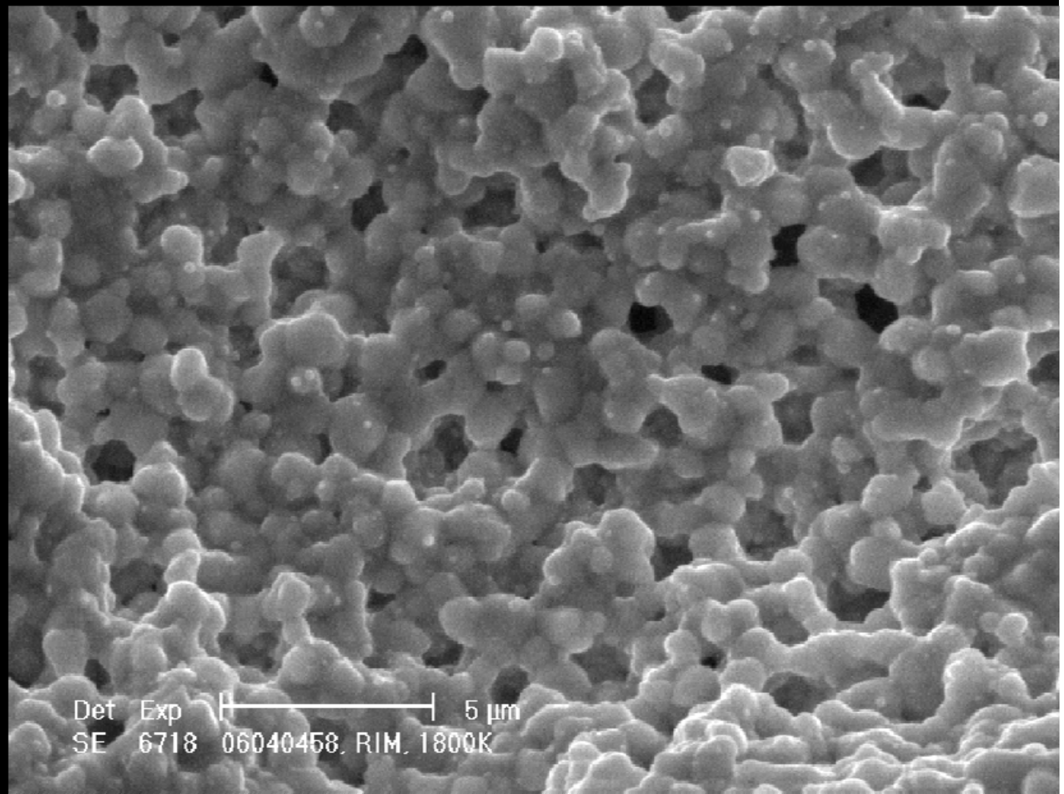
1800 K

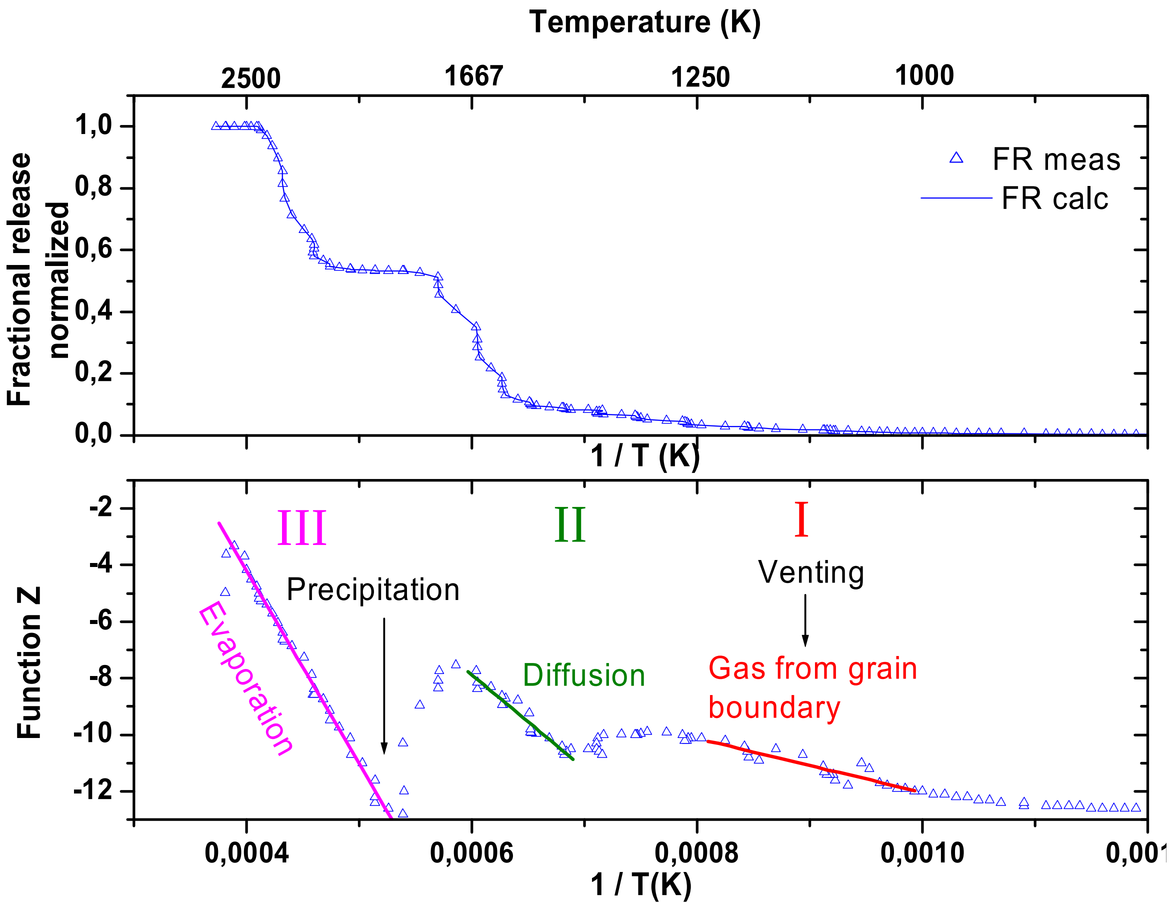


Zr
Pd
Mo
U
Rh
Ru
Tc
2.90
Zr
U
Pd
Rh
Mo
Ru
Tc
Ba
Ba
2.90
4.90
5 µm
4 06040458. RIM. 1800K



Det Exp
5 µm
SE 6718 06040458. RIM. 1800K

Analysis of Xe fractional release



Good agreement between FR_{meas} et FR_{calc}

Convolution function Z of FR

$$Z(1/T) = \ln\left\{\frac{d}{dt}\left[-\ln(1-FR)\right]\right\}$$

ΔH_{I} = 40 +/- 10 kcal /mol

ΔH_{II} = 95 +/- 5 kcal /mol

ΔH_{III} = 150 +/- 10 kcal /mol

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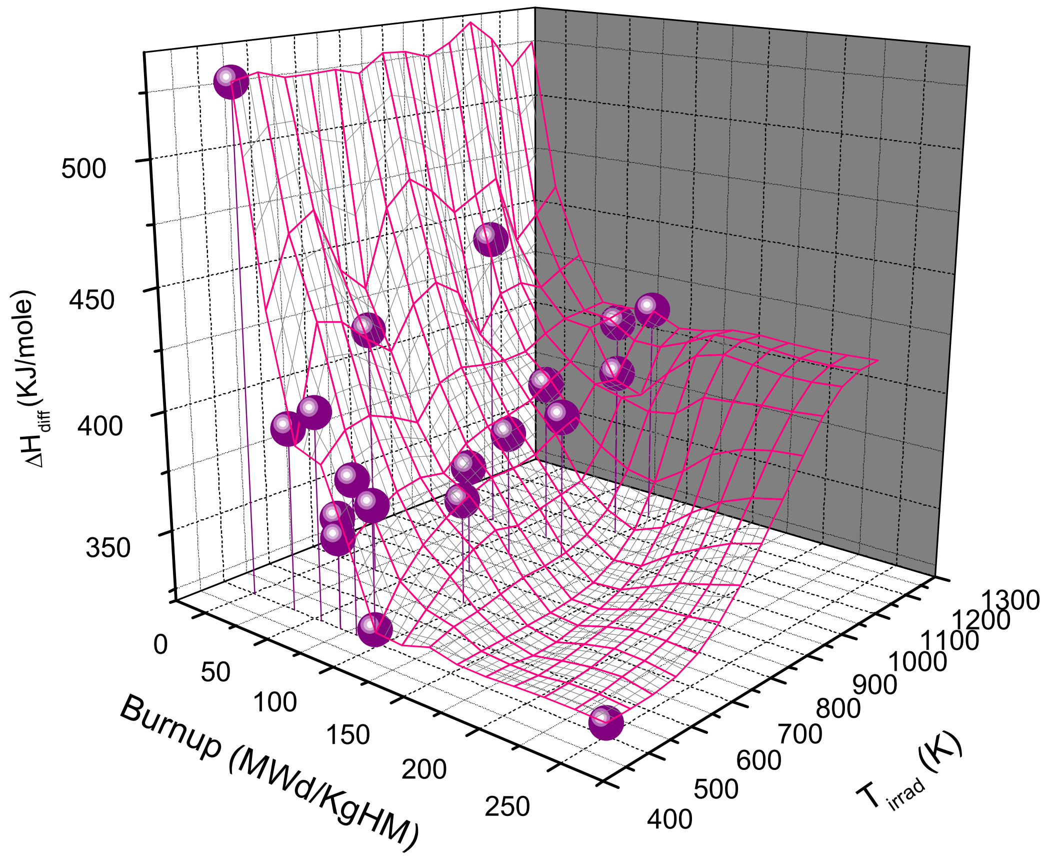
Diffusion enthalpy of Xe



IV - nitride fuels

Advanced fuels – context focus on nitrides

- Generation IV

Fast reactors fuel: (GenIV Roadmap – Dec 2002)

Generation IV System	Fuel				Recycle	
	Oxide	Metal	Nitride	Carbide	Advanced Aqueous	Pyroprocess
GFR[1]			S	P	P	P
MSR[2]						
SFR[3]	P	P			P	P
LFR		S	P		P	P
SCWR	P				P	
VHTR[4]	P				S	S

P: Primary option; S: Secondary option

[1] The GFR proposes (U,Pu)C in ceramic-ceramic (cercer), coated particles or ceramic-metallic (cermet).

[2] The MSR employs a molten fluoride salt fuel and coolant, and fluoride-based processes for recycle.

[3] The SFR has two options: oxide fuel with advanced aqueous, and metal fuel with pyroprocess.

[4] The VHTR uses a once-through fuel cycle with coated (UCO) fuel kernels, and no need for fuel treatment, as the primary option.

- Space propulsion reactor fuel

Characterization of MX fuels

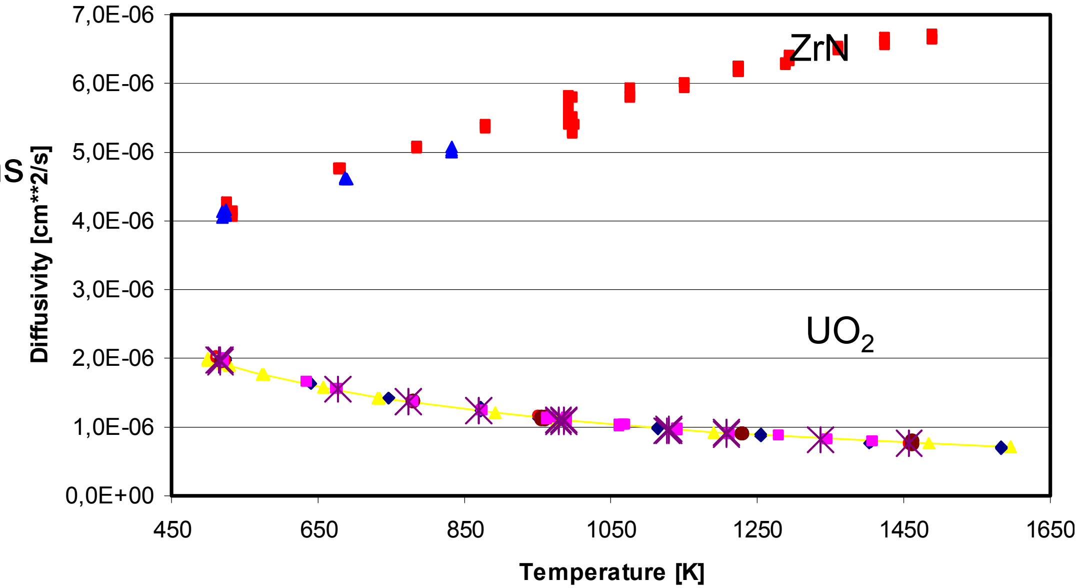
• First tests on UN, ZrN:
Investigations on (Zr,Pu)N
recently started

• Future work on
- unirradiated (U,Pu)N
- irradiated fuels from old campaigns

Properties

-thermal diffusivity
- specific heat
- vapour pressure
- hardness
- oxidation behaviour
- melting point
- thin films

Thermal diffusivity of ZrN (laserflash)



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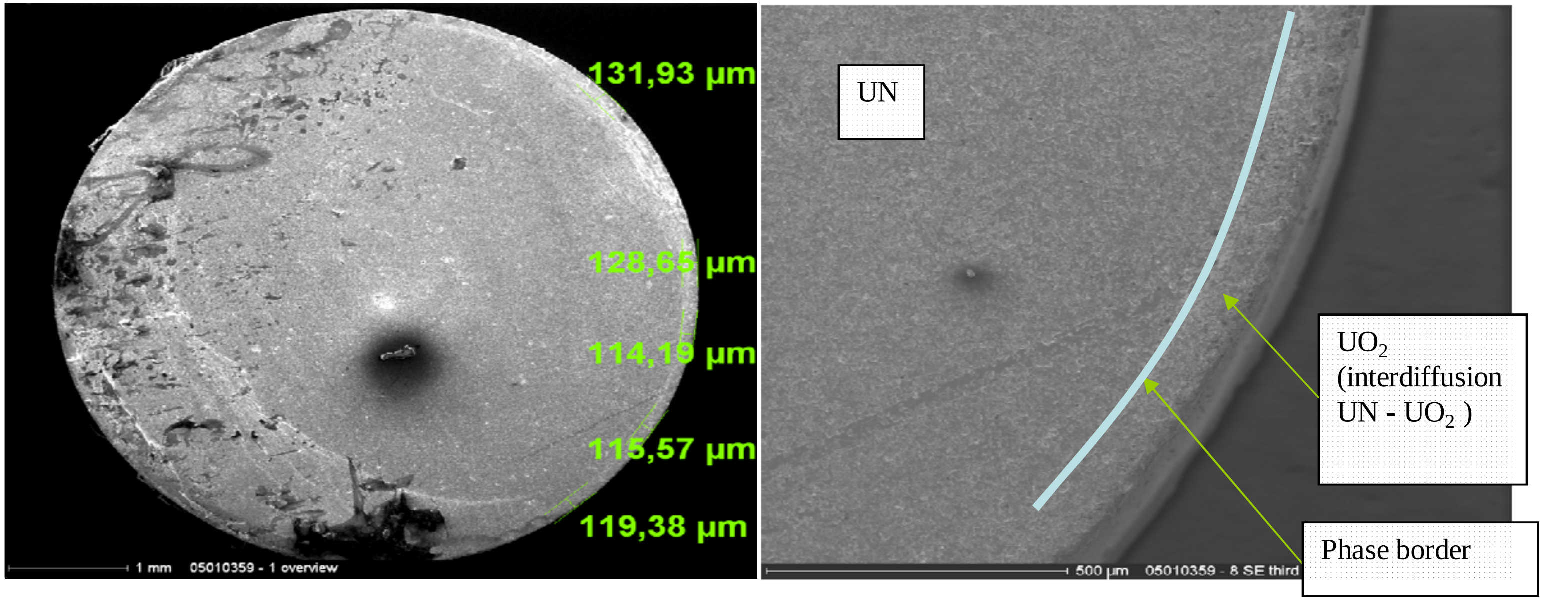
Phase analysis of UN

characterization of oxidation process



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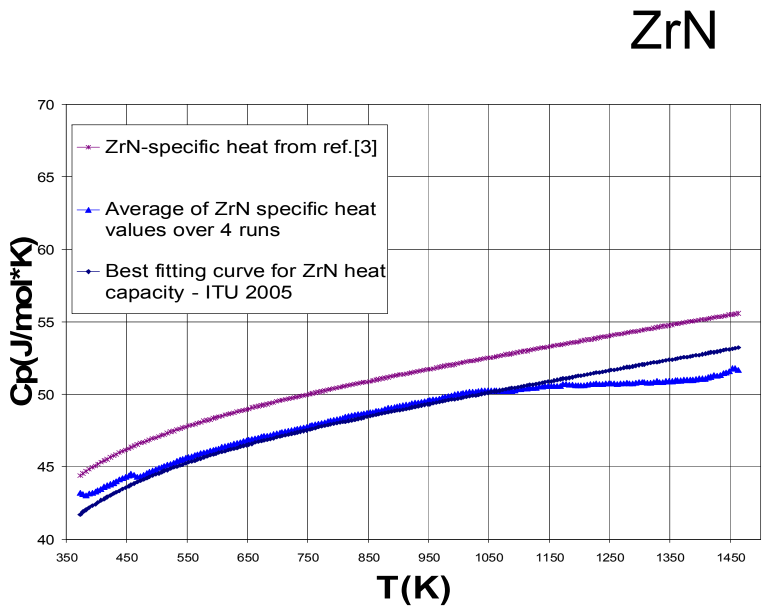
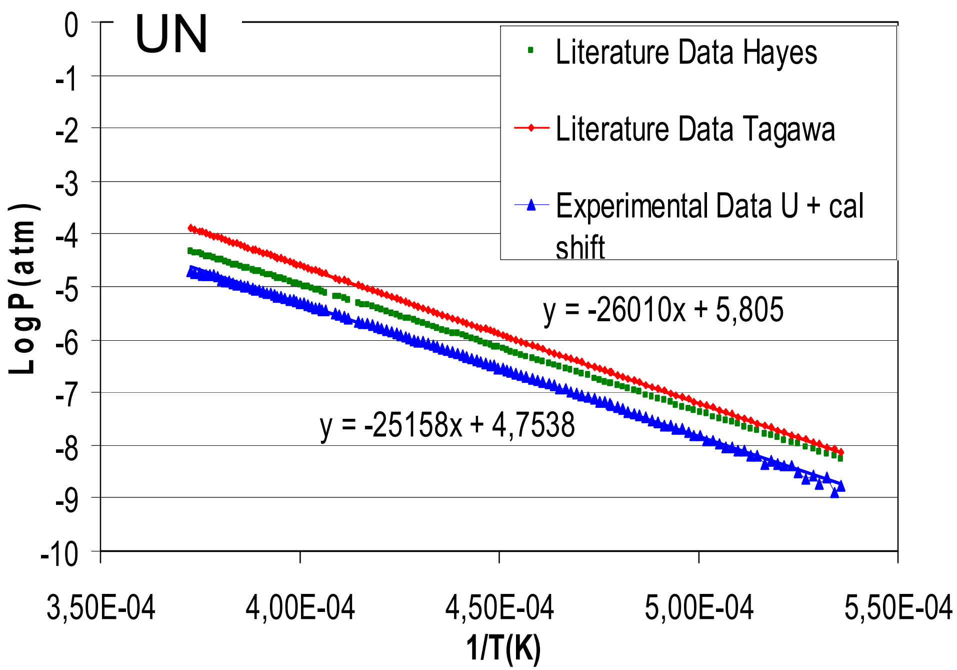
Thermodynamic properties of nitrides

Specific heat (DSC)



Vapour pressure of U (Knudsen cell)



within ~3% from literature curves

At T >1100 K solid state reaction between oxide and nitride

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Understanding basic mechanisms of damage formation

V - (U, 238Pu)O2

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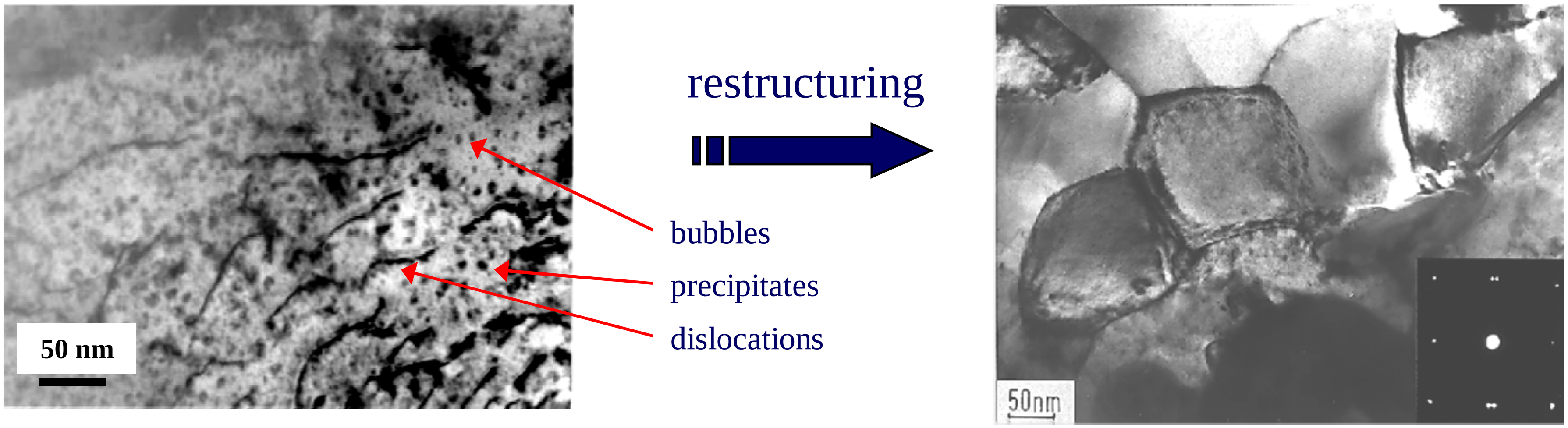
Phenomenological models, based on questionable assumptions, or incomplete:

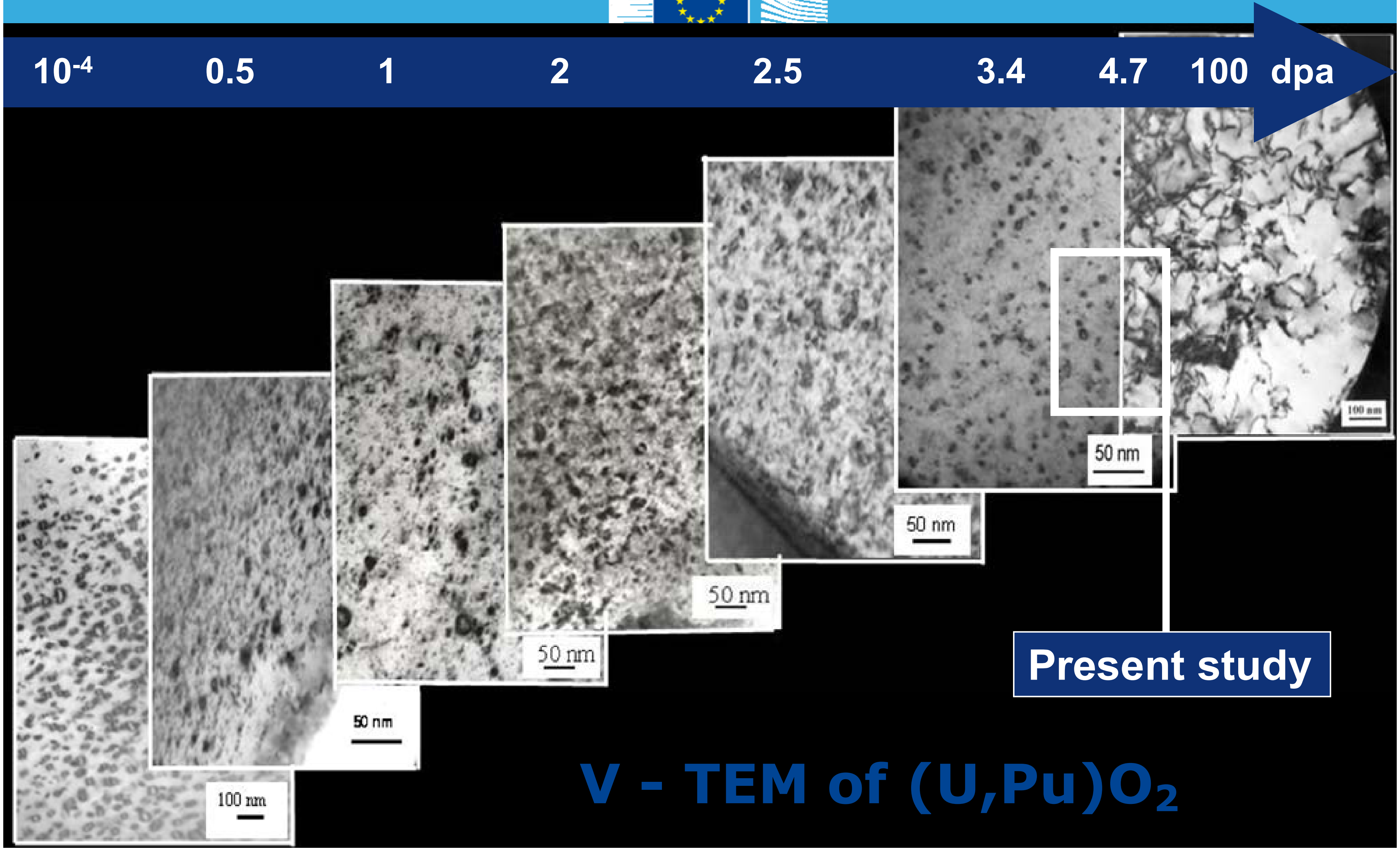
– role of dislocations ... not taken into account.

– « release » of total strain energy, associated with radiation defects . not calculated.



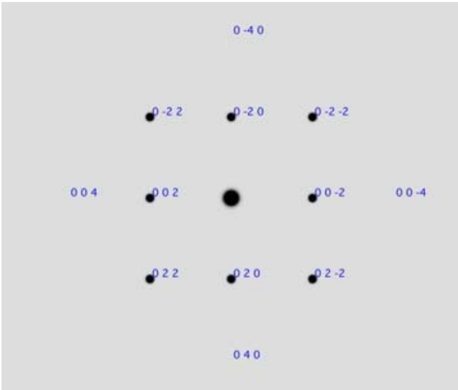
Observation (TEM micrographs) of the sub-grain boundary formation

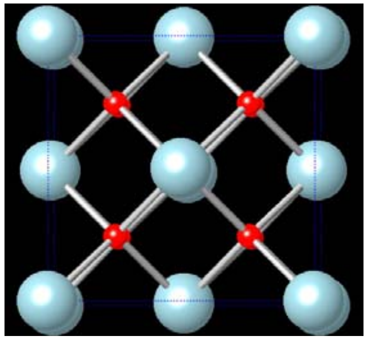
Dislocations are needed to form these new sub-grain boundaries ...

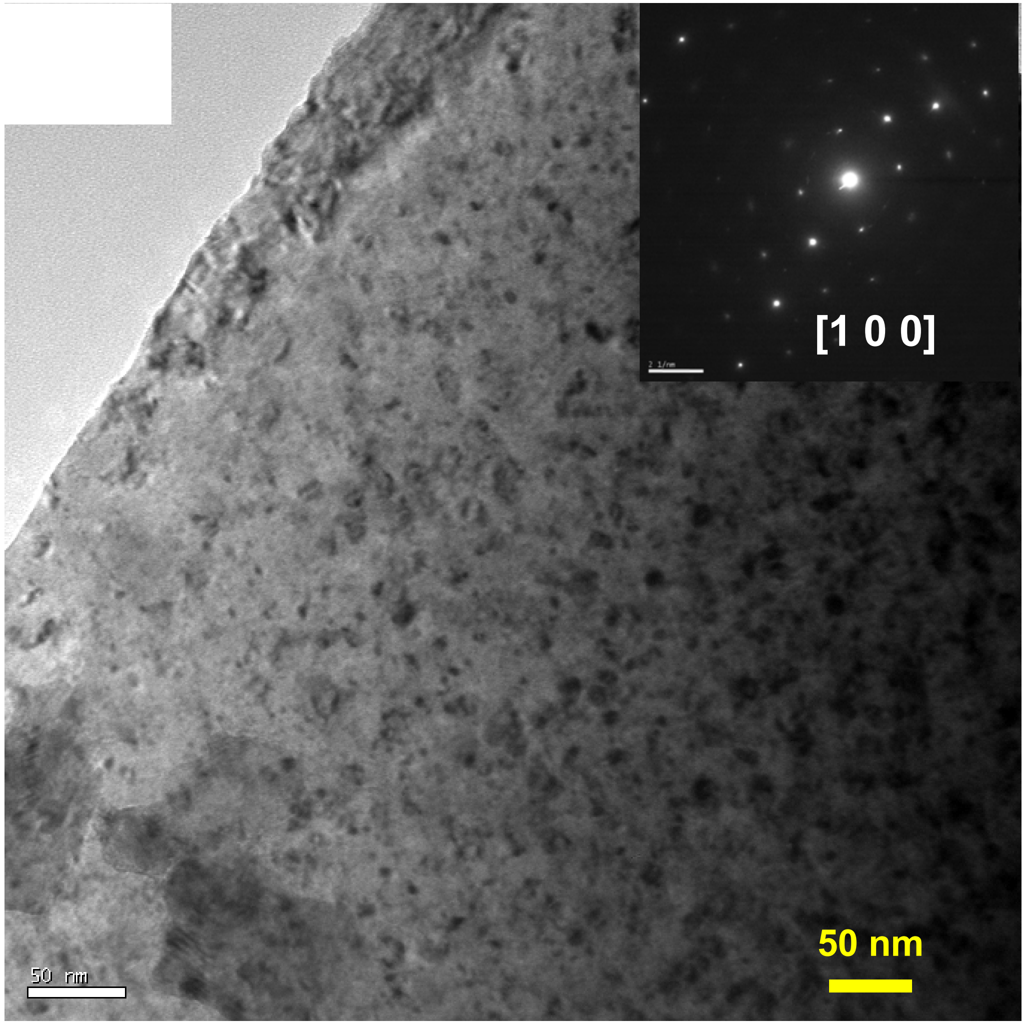


V - TEM of $(U,Pu)O_2$

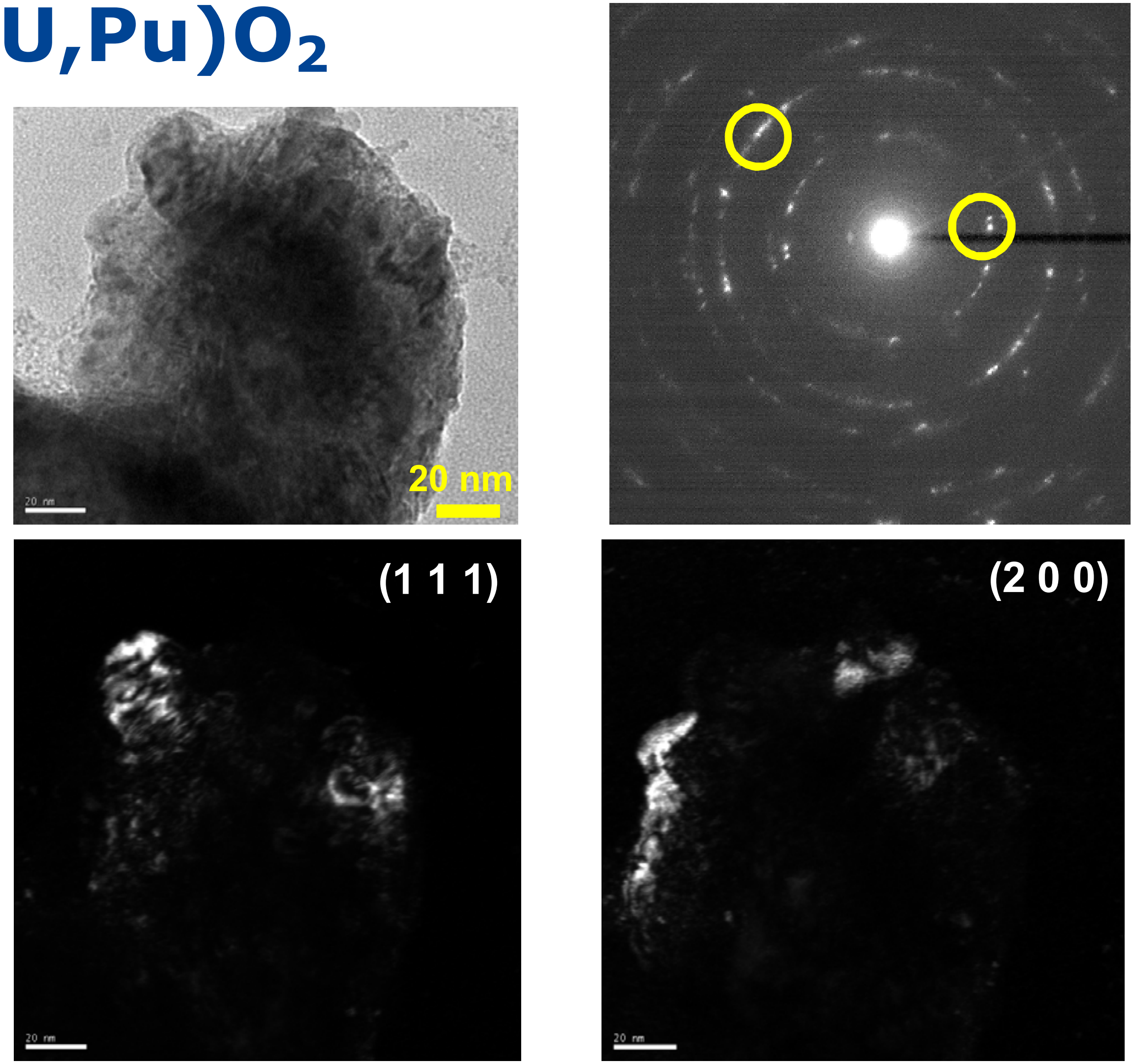
V - TEM of $(U,Pu)O_2$







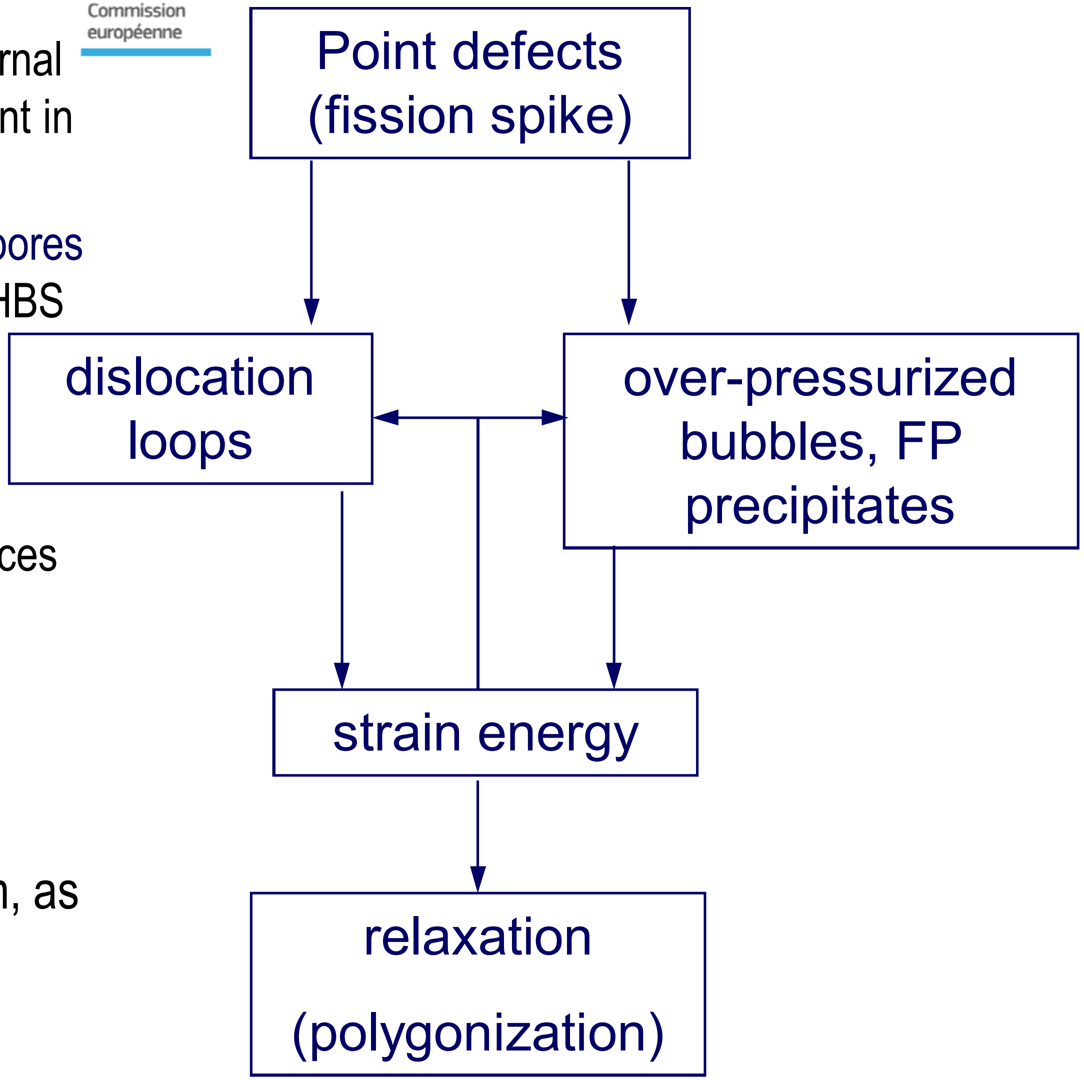
V - TEM of $(U,Pu)O_2$



Many different “heterogeneities” create internal stresses which have to be taken into account in the total strain energy:

- inclusions like precipitates, bubbles and pores (both as-fabricated and formed during the HBS formation) and the irradiation defects.
- the plastic deformation from one grain to another is responsible to internal stresses.
- the high temperature gradient which induces thermal strain.

When the **elastic energy** is sufficiently high, **polygonization is triggered**: the dislocations reorder themselves to form, as observed, low angle grain boundaries, reducing the energy of the system.



Conclusions

Combination of Mass Spectrometry and microstructure is efficient to understand the gas behaviour in fuels.

FGs are insoluble in the bulk and the thermally activated diffusion seems to be the main matter transport mechanism.

The release is strongly dependent on the irradiation history of the samples (burn-up, irradiation temperature) and their final micro-structure: grain size pore size and density, porosity, defects,….

FGs are mostly retained in the HBS.

Conclusions , cont‘d

- **Grain Boundaries act as effective sinks for defects.**
- **HBS-pores are stable and diminish gas-matrix swelling**
- **Nanocrystalline structure has superior mechanical properties:**

  - Superplaticity (Pellet Clad Interaction stress relieve)

  - Less cracking and fracture (but fragmentation by abnormal T increase !)
- **α-doped (^{238}Pu) UO_2 samples can reproduce <u>some</u> of the features observed during irradiation in a reactor (point defects, extended defects: dislocation loops and Helium bubbles)**
- **The polygonization process is observed in alpha-damaged samples**

Nuclear Fuel Development in the Future: Medium- & Long-term Objectives

⇨ Optimize Pu-U (Th) oxide fuels for existing LWRs and ALWRs:

- Fabrication process definition
- Fuel specifications
- Performance data-package

by:

- Irradiation testing
- Analyses
- Comparison to MOX data-base
- International collaborations

⇨ Develop U-Pu-Ma fuels that can be used in existing fast spectrum transmutation systems (~ 2020).

⇨ Determine feasible fuel options consistent with selected transmutation implementation scenario

by:

- Irradiation testing
- Analyses
- International collaborations

Aknowledgements

V. Rondinella, Hj. Matzke, R. Konings, J.-P. Hiernaut, H. Thiele, J.-Y. Colle, B. Cremer, R. Jardin, D. Bouxière, J. Cobos (ITU), R. Conrad (IE), N. Chauvin, J. Noirot, D. Roudil, X. Deschanels, P. Garcia (CEA),C. Thiriet-Dodane, P. Lucuta (AECL), W. Weber (PNNL), R.Schramm, F. Klaassen, K. Bakker (NRG), A. van Veen (IRI), AREVA, CRIEPI, GSI, GANIL

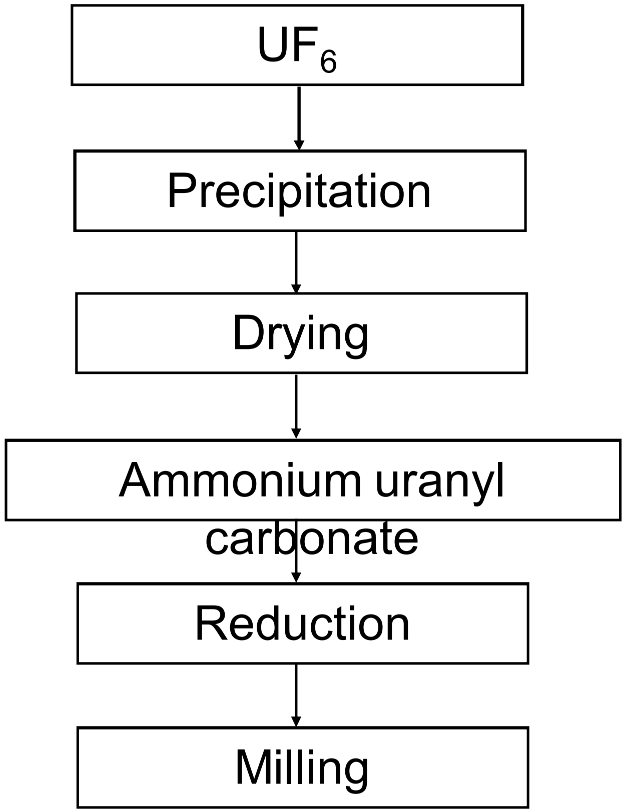
Preparation of ceramic grade UO_2 powder

The ADU process: aqueous process

UF_6	
↓	
Precipitation	$2UF_6 + 7H_2O + 2NH_3 \rightarrow (NH_4)_2U_2O_7 + 12HF$
↓	
Drying	
↓	
Ammonium di-uranate	$(NH_4)_2U_2O_7$
↓	
Reduction	$(NH_4)_2U_2O_7 \rightarrow U_3O_8 \rightarrow UO_2$
↓	
Milling	

Preparation of ceramic grade UO_2 powder

The AUC process: aqueous process



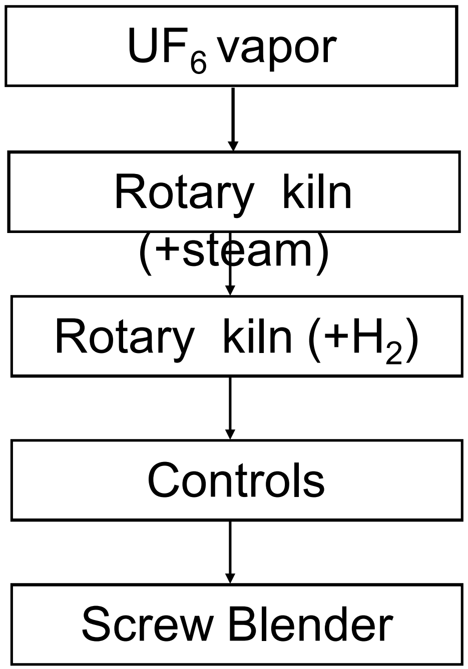
$$UF_6 + 5H_2O + 10NH_3 + 3\,CO_2 \rightarrow (NH_4)_4UO_2(CO_3)_3 + 6NH_4F$$

$(NH_4)_4UO_2(CO_3)_3$

$$(NH_4)_4UO_2(CO_3)_3 + H_2 \rightarrow UO_2 + 3CO_2 + 4NH_3 + 3H_2O$$

Preparation of ceramic grade UO_2 powder

The IDR process: integral dry route



$$UF_6 + 2H_2O\ (vap) \rightarrow UO_2F_2(sol) + 4HF$$

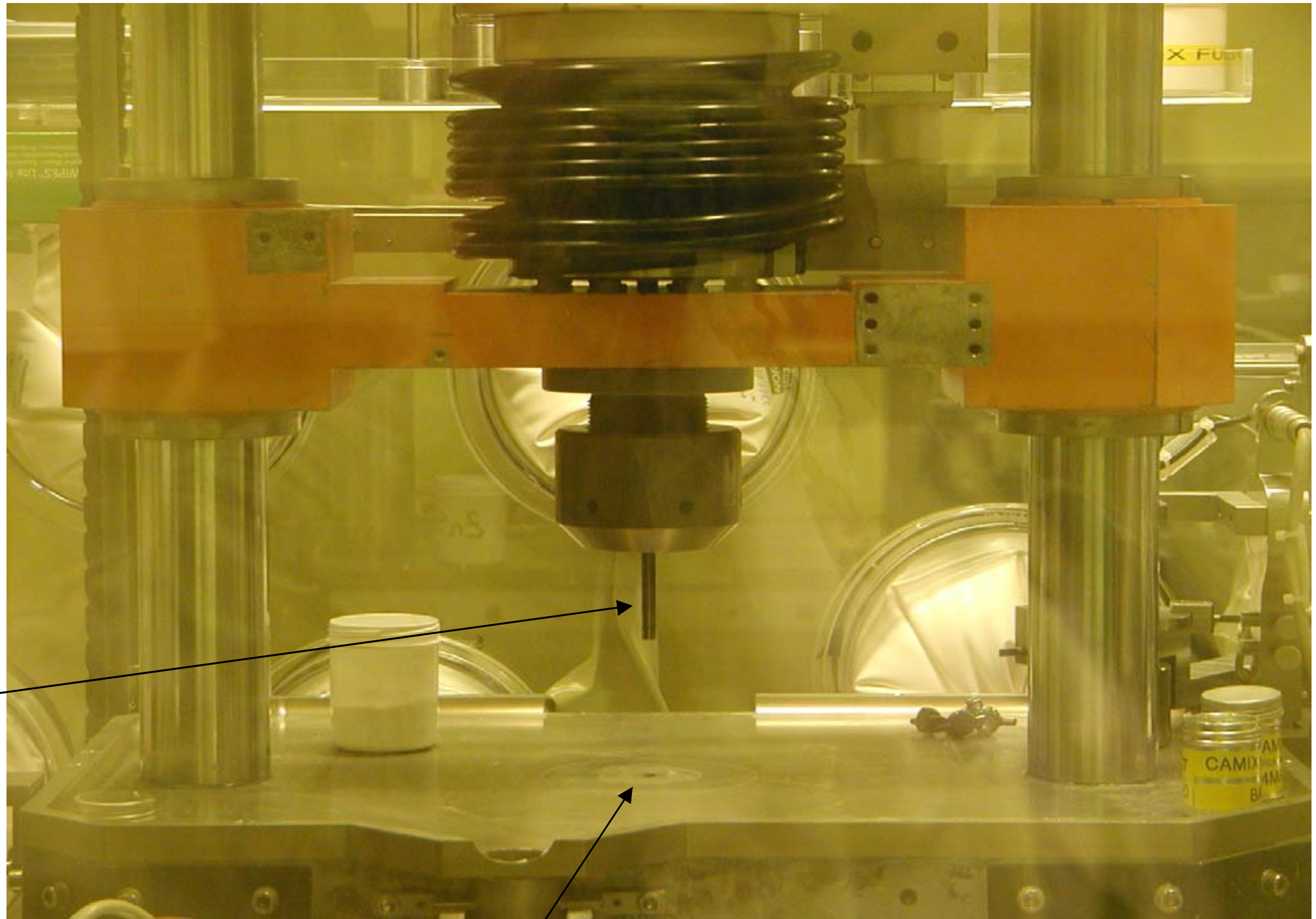
$$UO_2F_2(sol) + H_2O \rightarrow UO_3 + 2HF$$

$$UO_3 + H_2 \rightarrow UO_2 + H_2O$$

Preparation of ceramic grade UO_2 powder

	IDR	ADU	AUC
Specific surface (m^2/g)	2.5-3.0	2.8-3.2	5.0-6.0
Raw density (g/cm^3)	0.7	1.5	2.0-2.3
Tap denisty (g/cm^3)	1.65	2.4-2.8	2.6-3.0
Mean size (microns)	2.4	0.4-1.0	8
Morphology	dendrites	spheroids	Porous aggl.
O/U ratio	2.05	2.03-2.17	2.06
Fluor (ppm)	<25	30-50	30-70
Carbon (ppm)	20	40-200	120
Iron (ppm)	10	70	10-20
Boron (ppm)	<0.05	0.2	0.1

Densification of UO_2 pellets by sintering

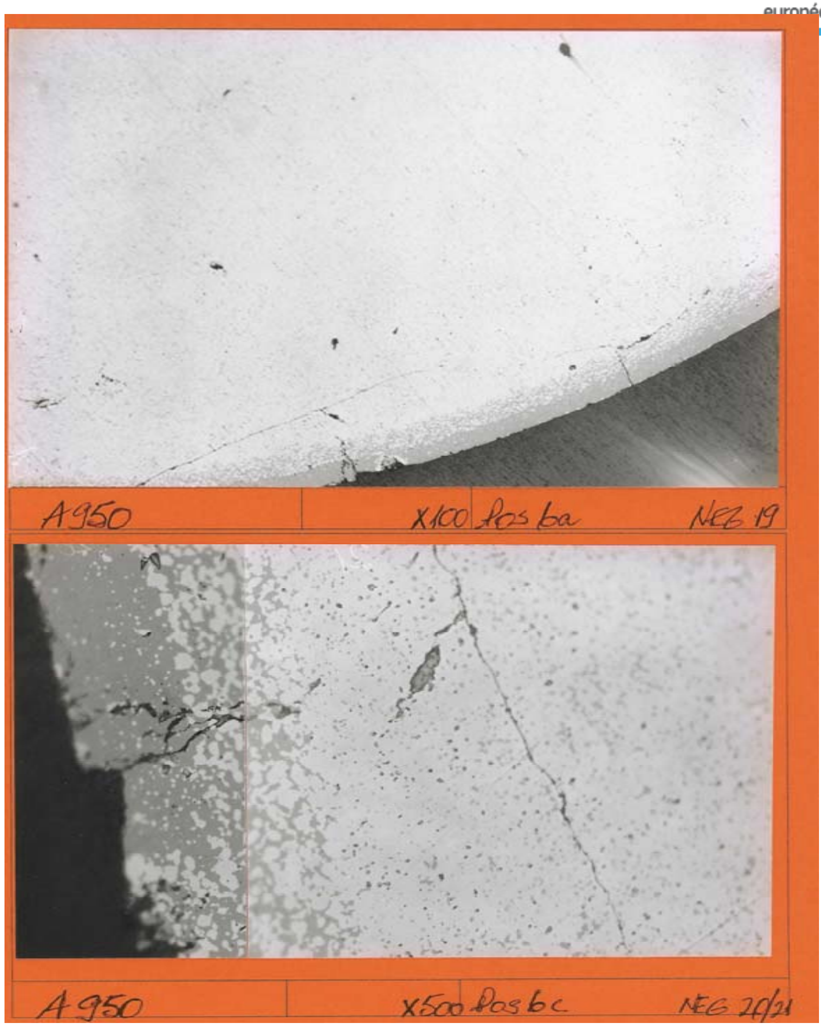


Piston

Matrix

Phase analysis of UN

(ceramography)

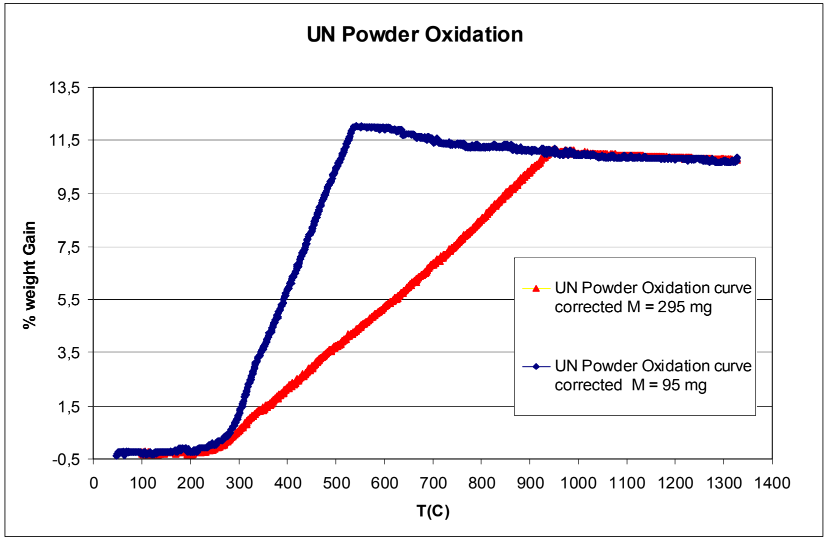


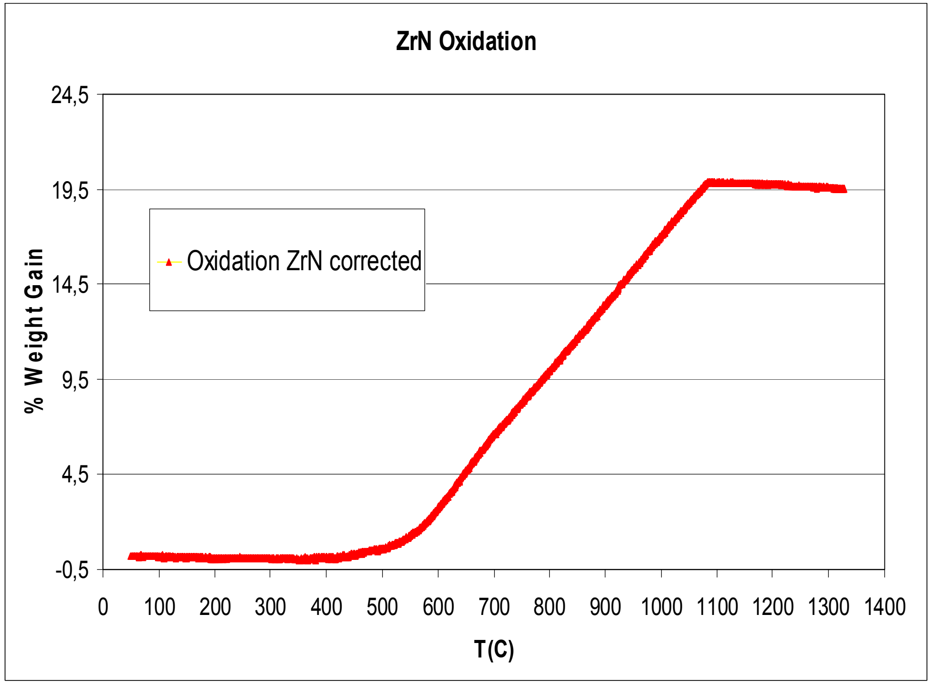
oxidized phase present also in bulk

Commission européenne

Oxidation curves
(TG)

critical temperatures for ZrN e UN (confirm published data)



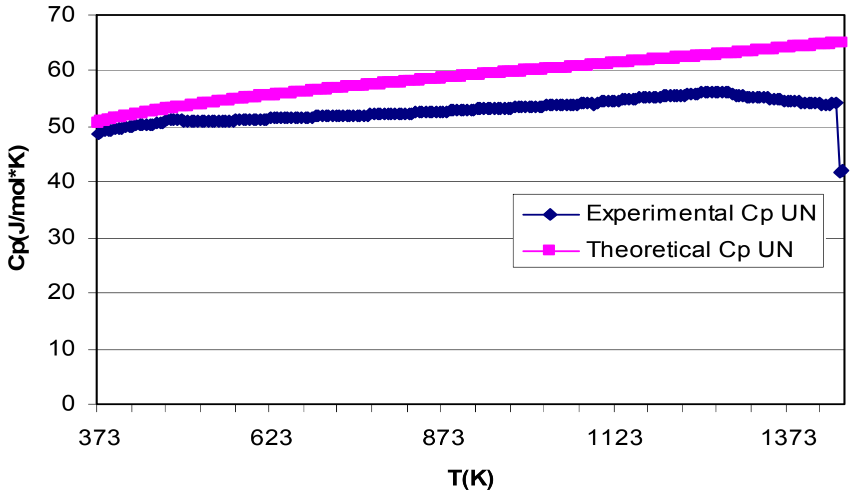


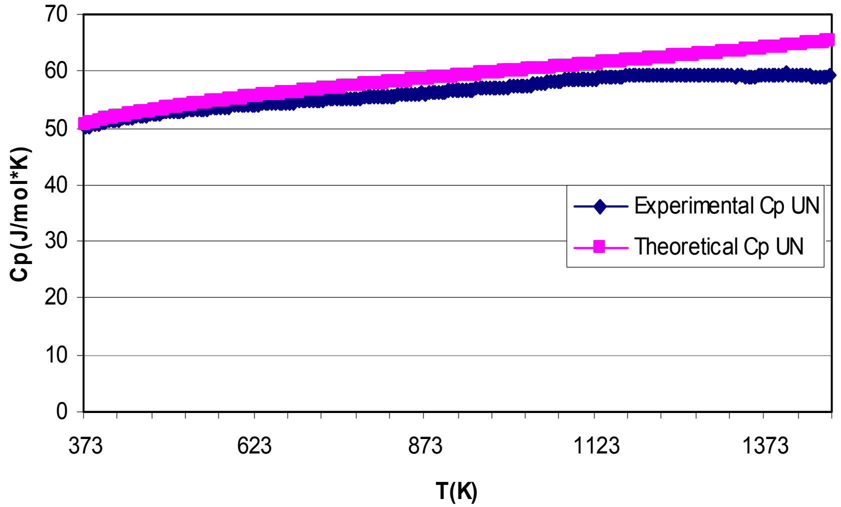
Characterization of nitride fuels

Cp (DSC)

Commission européenne

- oxygen content in samples must be characterized
- implement new systems to obtain low O_2 in glove boxes
- adapt high-T techniques to oxygen-free conditions
- optimize sample handling and treatment





- oxidation and high T reactions
- optimization of experimental procedure.

Hardness

Vickers indentation

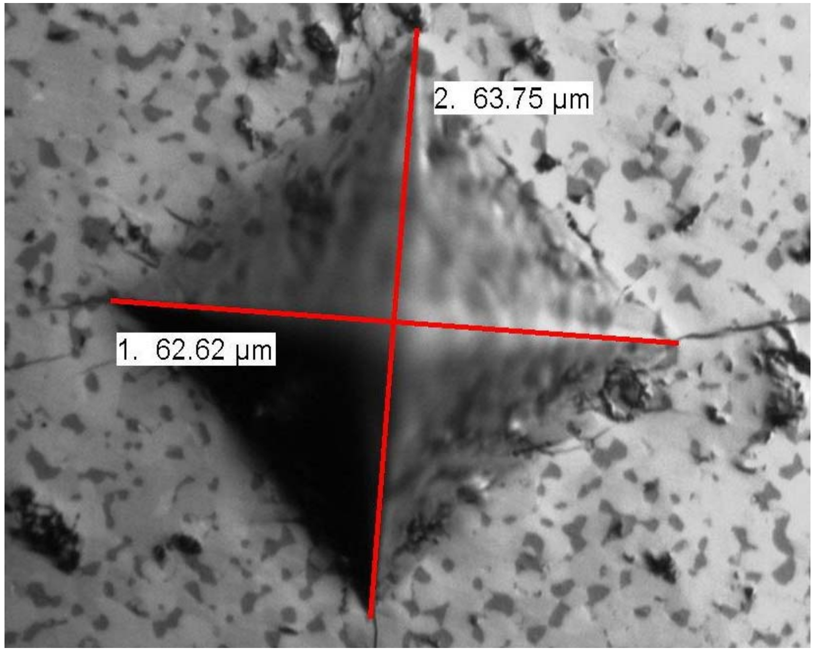
Commission européenne

Macro – Indenter (Material Hardness)

HV(UN experimental) = 690 kg/mm^2

HV(UN theoretical) = 450 (600) kg/mm^2

HV(UO_2theoretical) = 550 – 600 kg/mm^2



Working Conditions:

Load = 1.5 Kgf

room temperature

fuel research will continue to prepare data for selection studies

- Longer development time needed because fuels containing MA have not been developed before.
- Strong international collaboration is essential for selection studies.
- Availability of a fast-flux irradiation capability to test high-burnup fuels.
- A stronger integration with GEN IV and other programs concerning fuel needs must be achieved early in the fuel development programme.

back to the original assignment?
ITU past irradiation campaigns of advanced fuel

Commission européenne

DOUNREAY FR

DS1
Stoichiometry optimization of LMFBR MO_2

DS2
Smeared density optimisation of MO_2 at high burnup

RAPSODIE FR

DN1
optimisation of LMFBR MX fuels (MC, MCN, MCO, MN)
Na- and He-bonding

DN2
High burnup behaviour (MC, MCN, MCO, MN)
Na- and He-bonding

SILOE

GOCAR
T-dependence of swelling
NC, MCN, MCO, MN

PHENIX FR

NIMPHE
High burnup MC
In Na-bonding

BR2

POM
Transmutation of AmO_2

FACT/SUPERFACT
Transmutation of AmO_2

POM I-VII
Behaviour of UO_2 at very high burnups

HFR

NILOC
Smeared density optimisation
MC and MN

Joint Research Centre

MA bearing transmutation advanced fuels to be used in fast-spectrum transmuters (ADS, GEN IV)

Advanced high-burnup fuels for GEN IV reactors

Fertile-free fuel
➔ Fast reactors with inhomogeneous core

TRU-Rich fuel
➔ Fast reactors with low conversion ratio

Fertile-rich fuel
➔ high-burnup equilibrium fuel cycle (GEN-IV)