ISOLDE Workshop and Users meeting 2021

14-16 December 2021

Oxidation kinetic studies for the treatment and disposal of current and future UC_x target materials

Nhât-Tân Vuong
CERN (SY-STI-RBS)
EPFL (SB-ISIC-LIMNO)
14-12-2021

Types of target materials

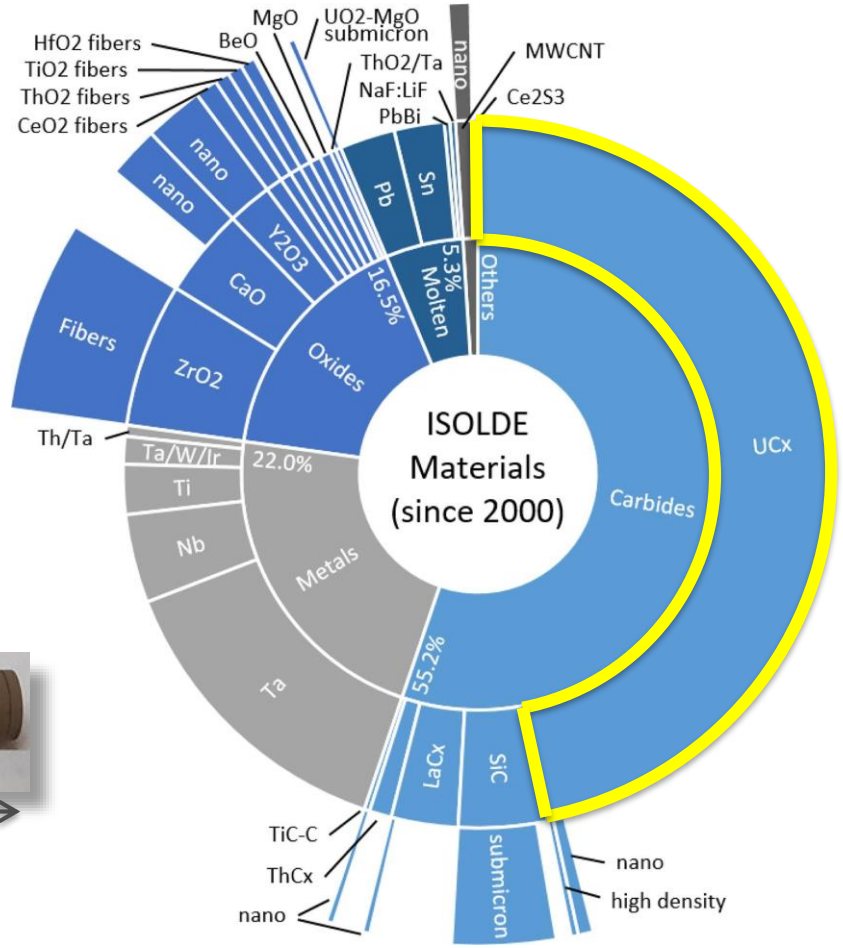
ISOLDE target unit

> 60% of beam time

UC_x pellets

15 mm

200 mm

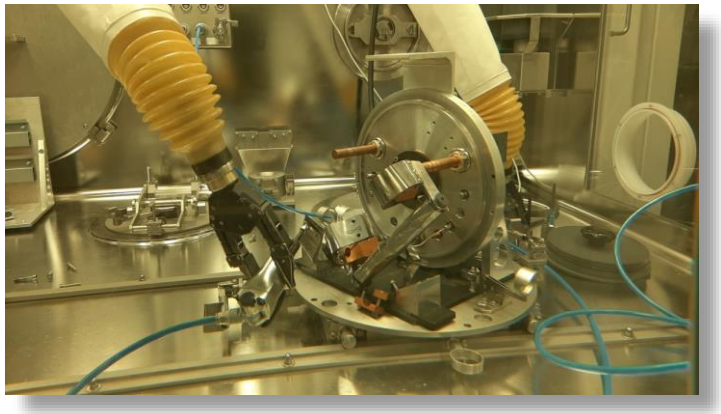


Target disposal

18 target/year
(>60% UC_x)

20+ years
300+ targets

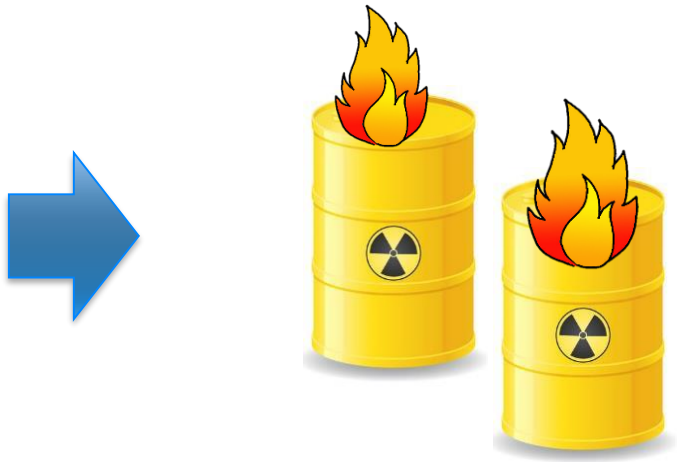
ISOLDE hot cell



Target dismantling starting 2022

UC_x target materials: Not suitable for long-term storage

Uranium carbide (UC_x) pellets



GLOBALLY HARMONIZED SYSTEM OF CLASSIFICATION AND LABELLING OF CHEMICALS (GHS)

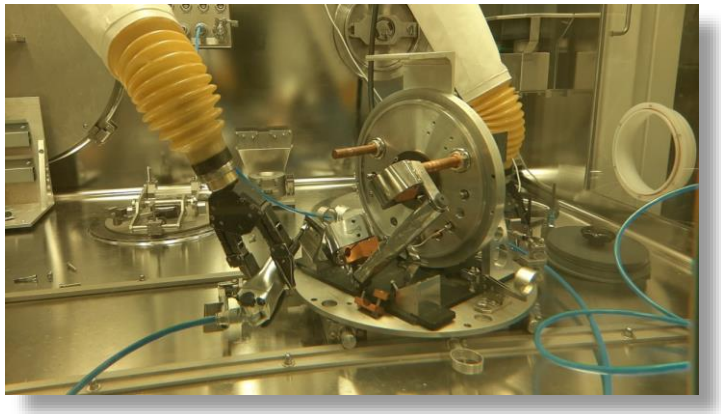
Definition:
A *pyrophoric solid* is a solid which, even in small quantities, is **liable to ignite** within five minutes **after coming into contact with air**.

Target disposal - UC_x

18 target/year
(>60% UC_x)

20+ years
300+ targets

ISOLDE hot cell



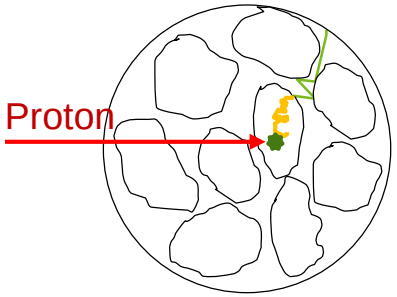
UC_x pellets

Oxidation

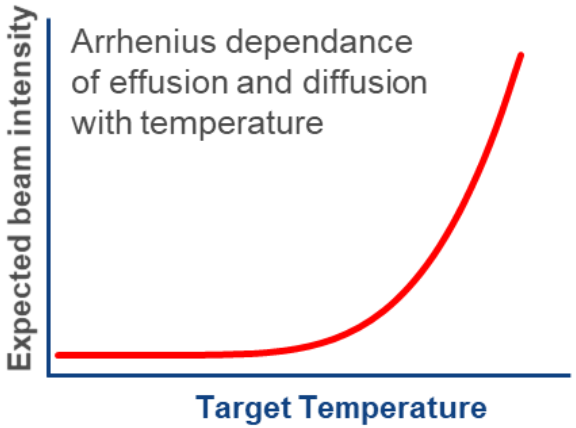
U_3O_8 powder

Microstructure vs isotope release

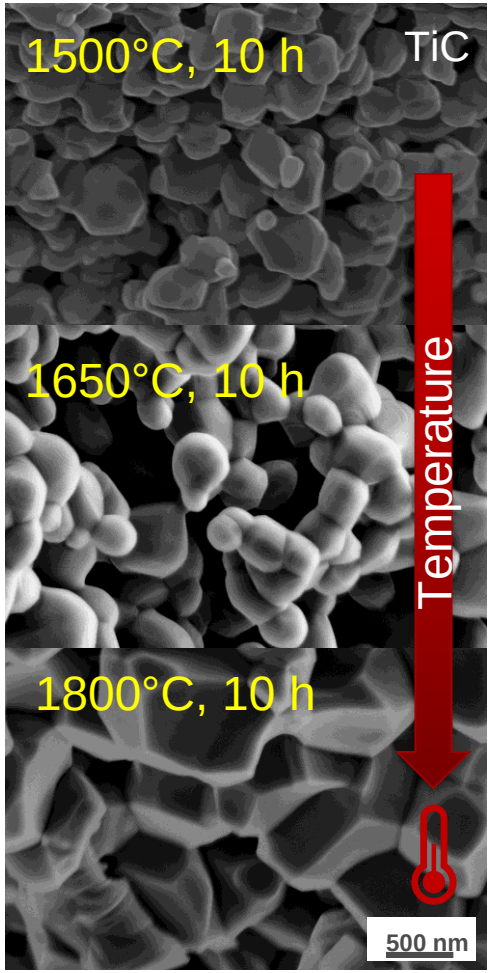
Isotope beam extraction



Diffusion
Effusion



Sintering

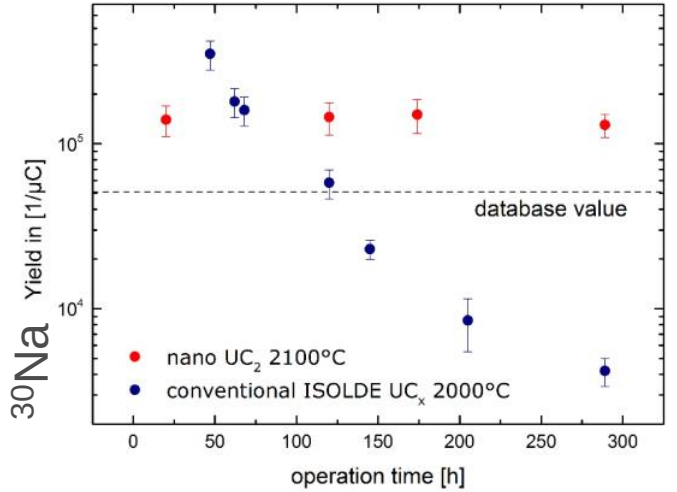


Target material engineering

Grain size (nano) ↘

Porosity ↗

Beam intensity vs time



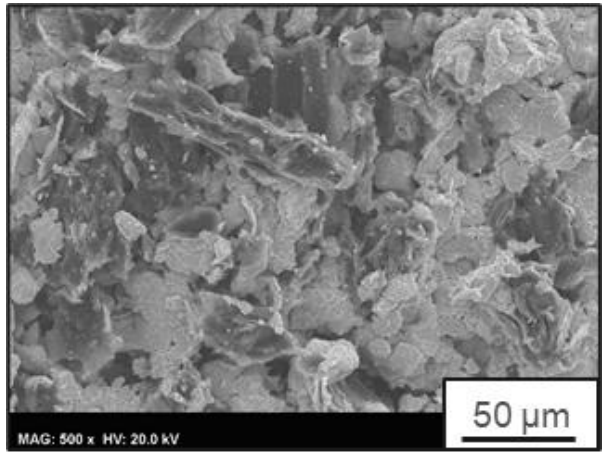
Nano-UC$_x$ prototype

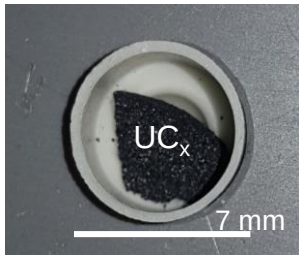
Micro-UC$_x$

Pyrophoricity of UC_x target materials

Micro-UC_x

15 mm

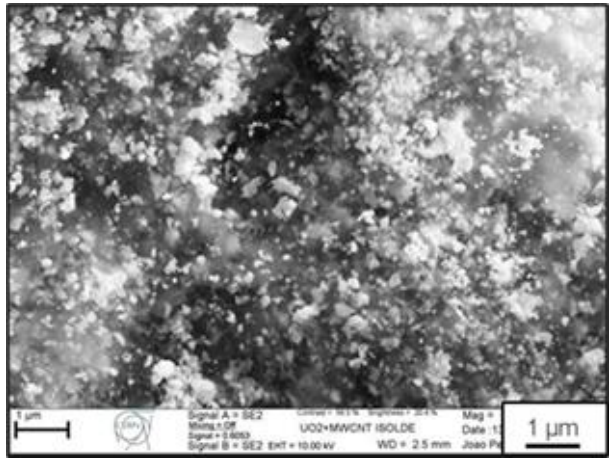


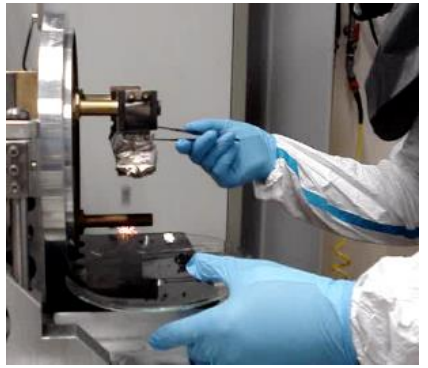


Stable in air
at room temperature

Nano-UC_x

15 mm





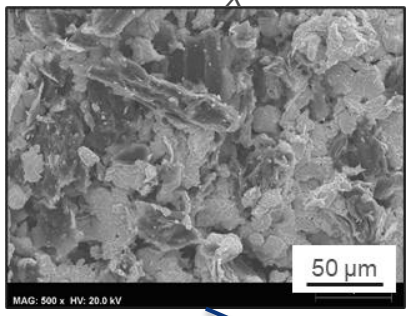
Falling *Nano-UC_x* pills

SEM images ack: Micro-UCx, I.D. Nogueira; Nano-UCx, J.P. Ramos

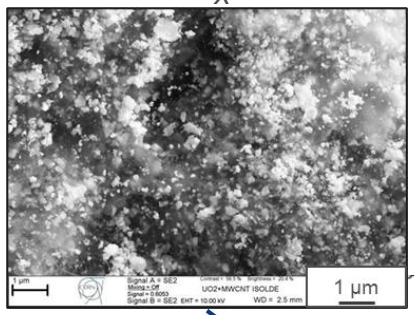
Micro- and nano-structured UC_x materials development

2014 J.P. Ramos, A. Gottberg

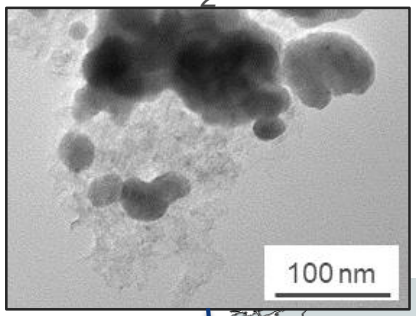
Micro-UC_x



Nano-UC_x



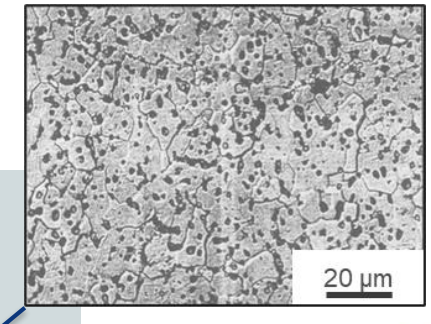
Nano-UC_2



European Commission
JOINT RESEARCH CENTRE

2019
O. Walter, K. Popa

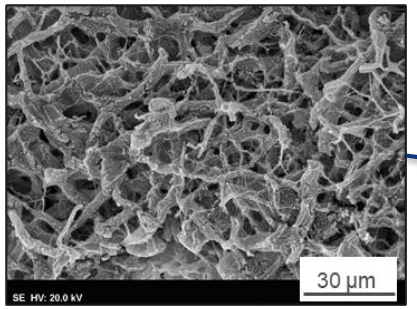
HDUC



Supplier:
Luch scientific
Rosatom

ROSATOM

UC_x-Nanofibers

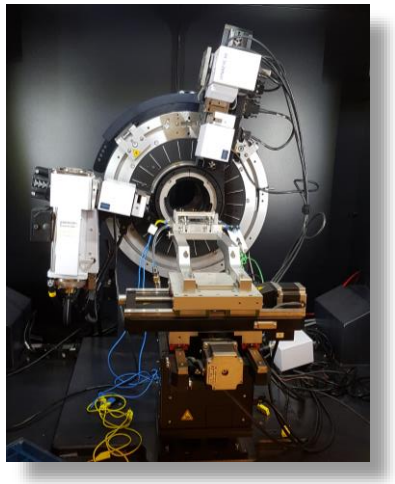


C²TN TÉCNICO LISBOA

2018
S. Chowdhury

Oxidation kinetics studies

Material characterization



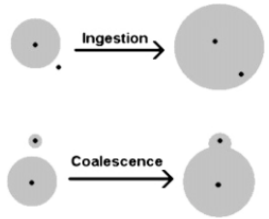
E-XRD
SEM
TEM
XPS
BET

Thermal analysis

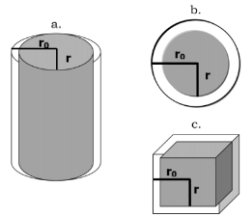
TGA-DTA-MS
Chemisorption analysis

Kinetics analysis

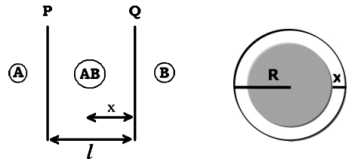
Nucleation & nuclei growth



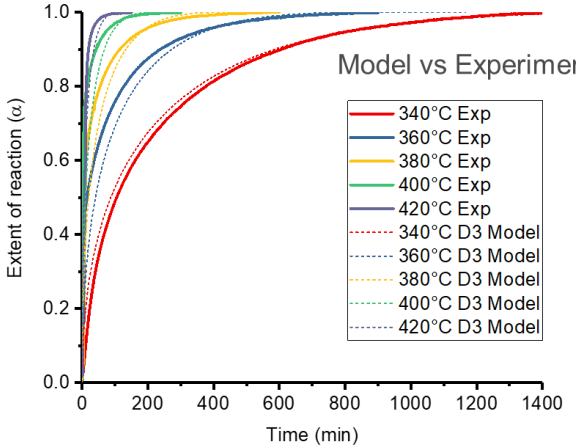
Surface area



Diffusion (D)

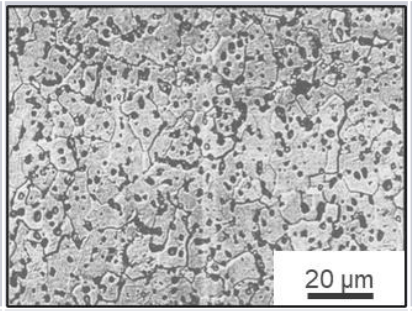
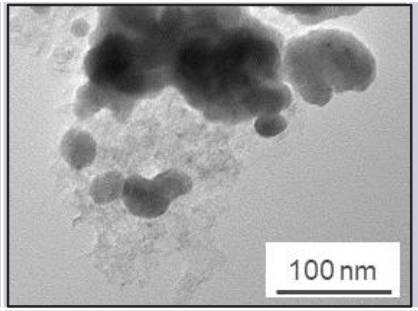
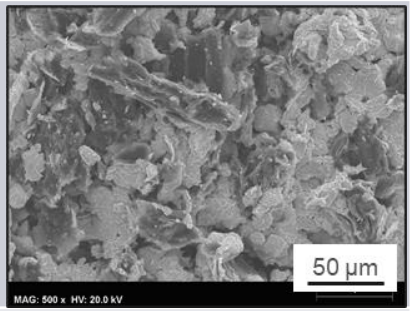
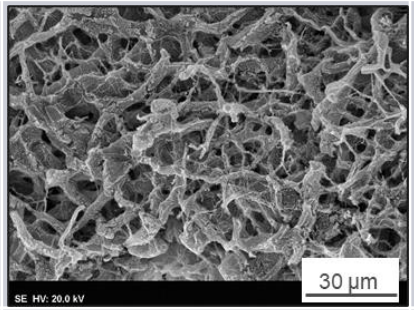
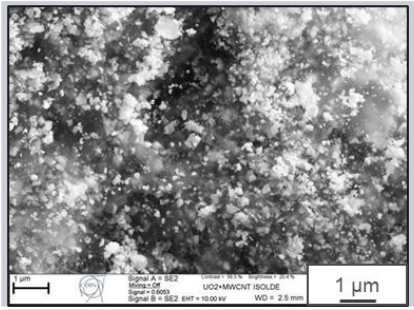


Model prediction



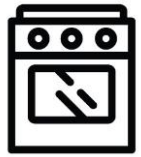
Rate, activation energy, mechanism

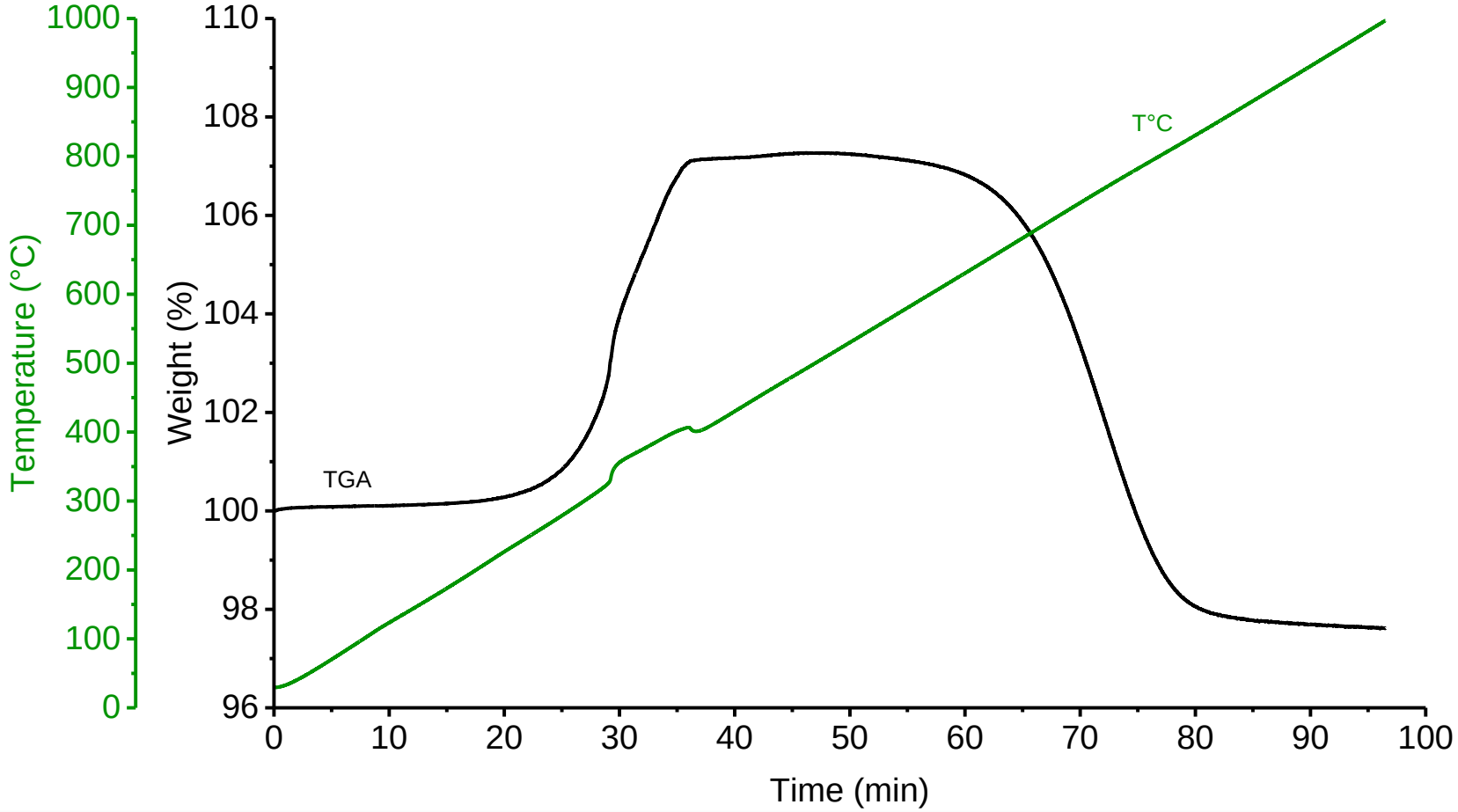
Characteristics of micro- and nano-structured UC_x

Materials / Characteristics		High Density UC	Nano UC_2	Micro UC_x	Nanofibrous UC_x	Nano UC_x
SEM/TEM						
Key characteristics		Dense UC pellet	Nano-powder High carbide phase purity >98% UC_2	Porous UC_2 + C composite pellet	Porous Nanofibers Large excess of C	Highly porous pellet Bimodal Size distribution High surface area
Phase composition [% wt]	UC UC_2 UO_2 C	76.9 10.8 12.3 0	0.9 86.5 0 12.6	3.6 86.7 0 9.8	0 34.6 14.8 50.6	Expect. similar to *Micro-UC_x*
Grain size		6 ± 3 µm	27 ± 8 nm	20-50 µm	4-10 nm (UC_2) TEM	160 nm and 2 µm UO_2
Density [g/cm³]		12.7	-	3.5 ± 0.8	-	1.4
C/$UC_{x,\ (1<x<2)}$		0	3.14	2.36	22.7	2.88
SSA [m²/g]		2.2	-	0.9	-	221

TGA

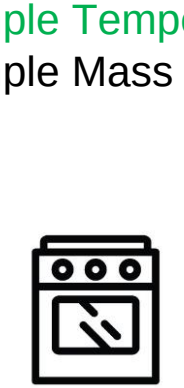
Sample Temperature
Sample Mass

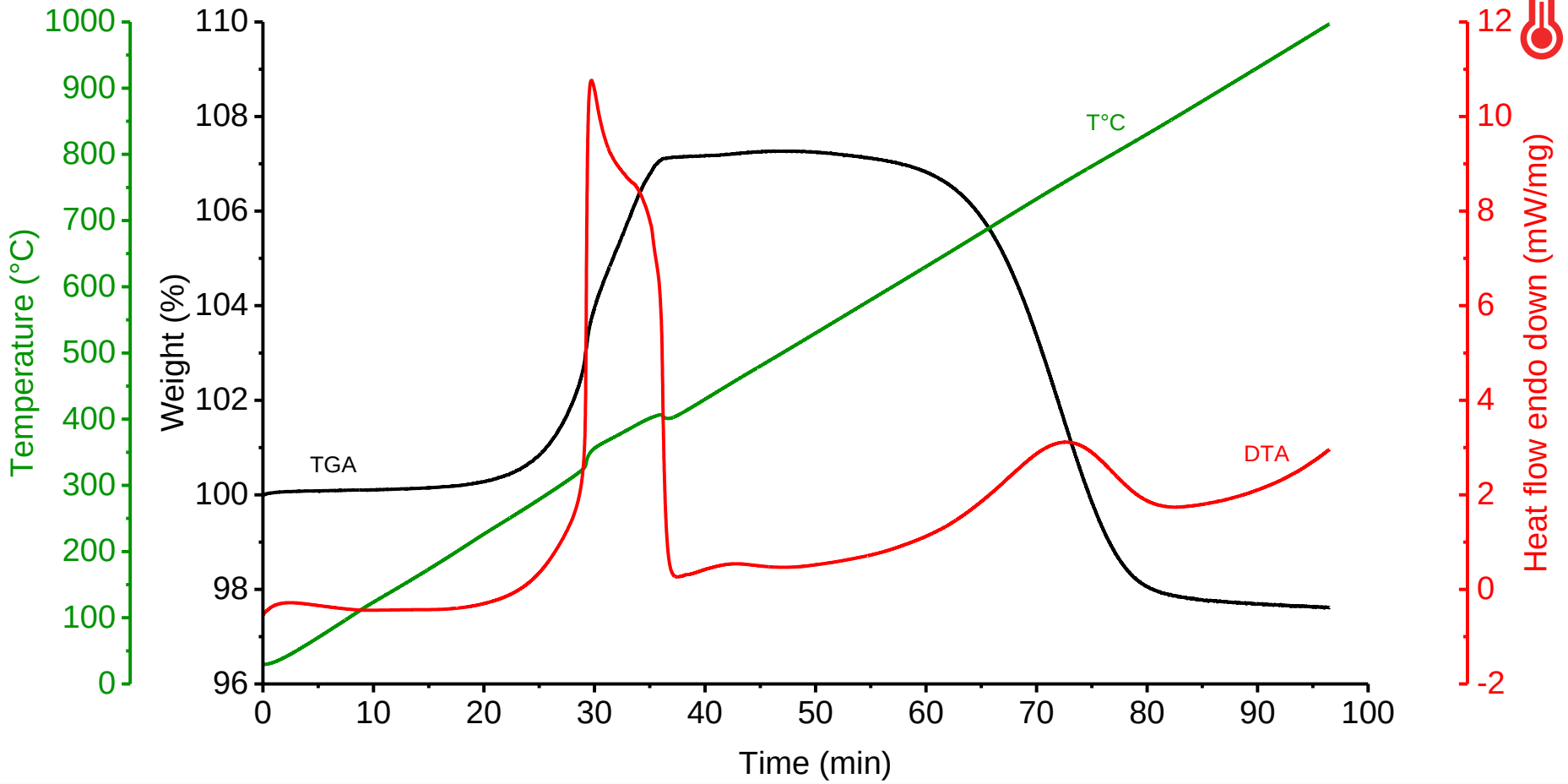




TGA-DTA

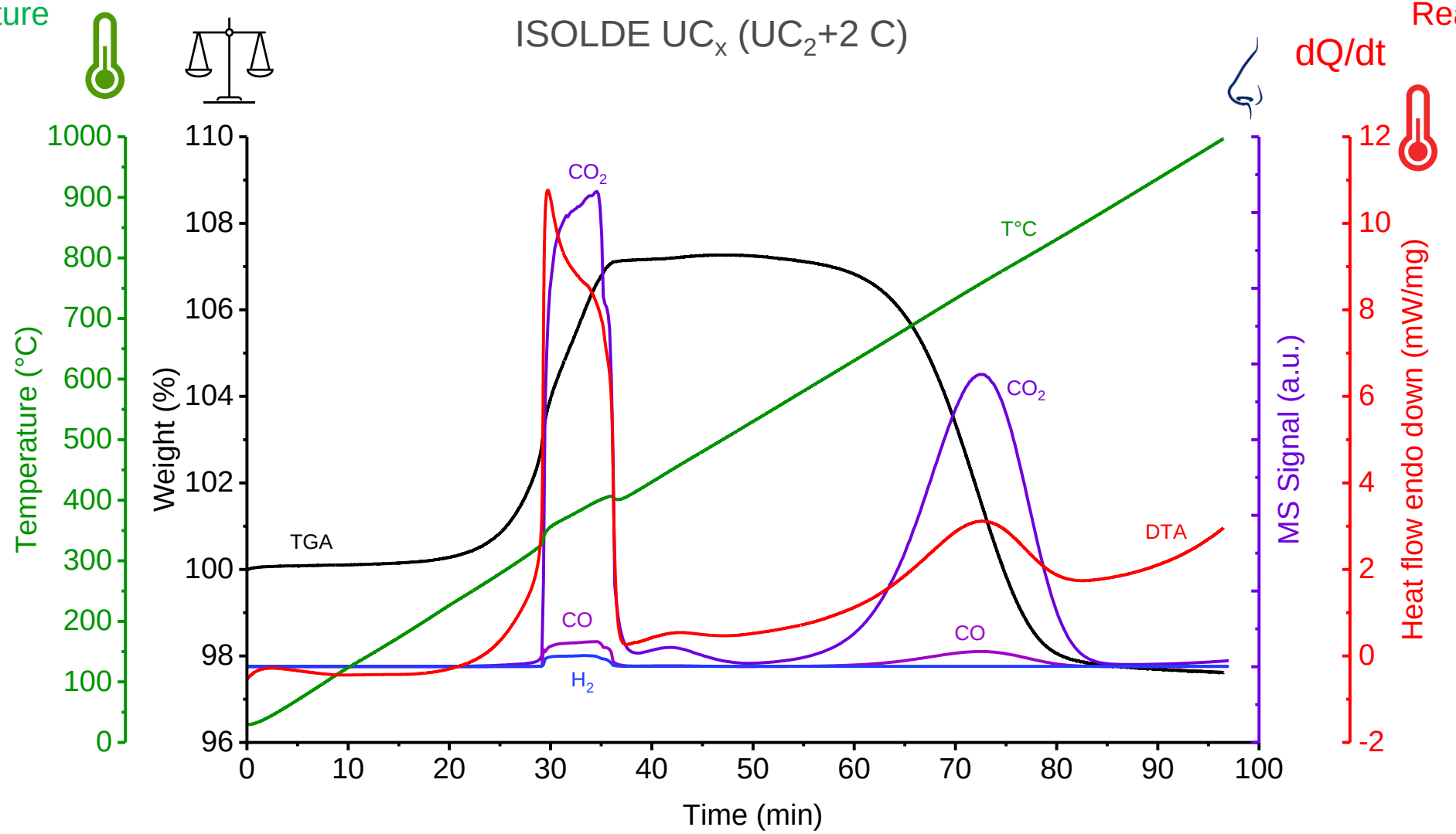
Sample Temperature
Sample Mass





TGA-DTA-MS

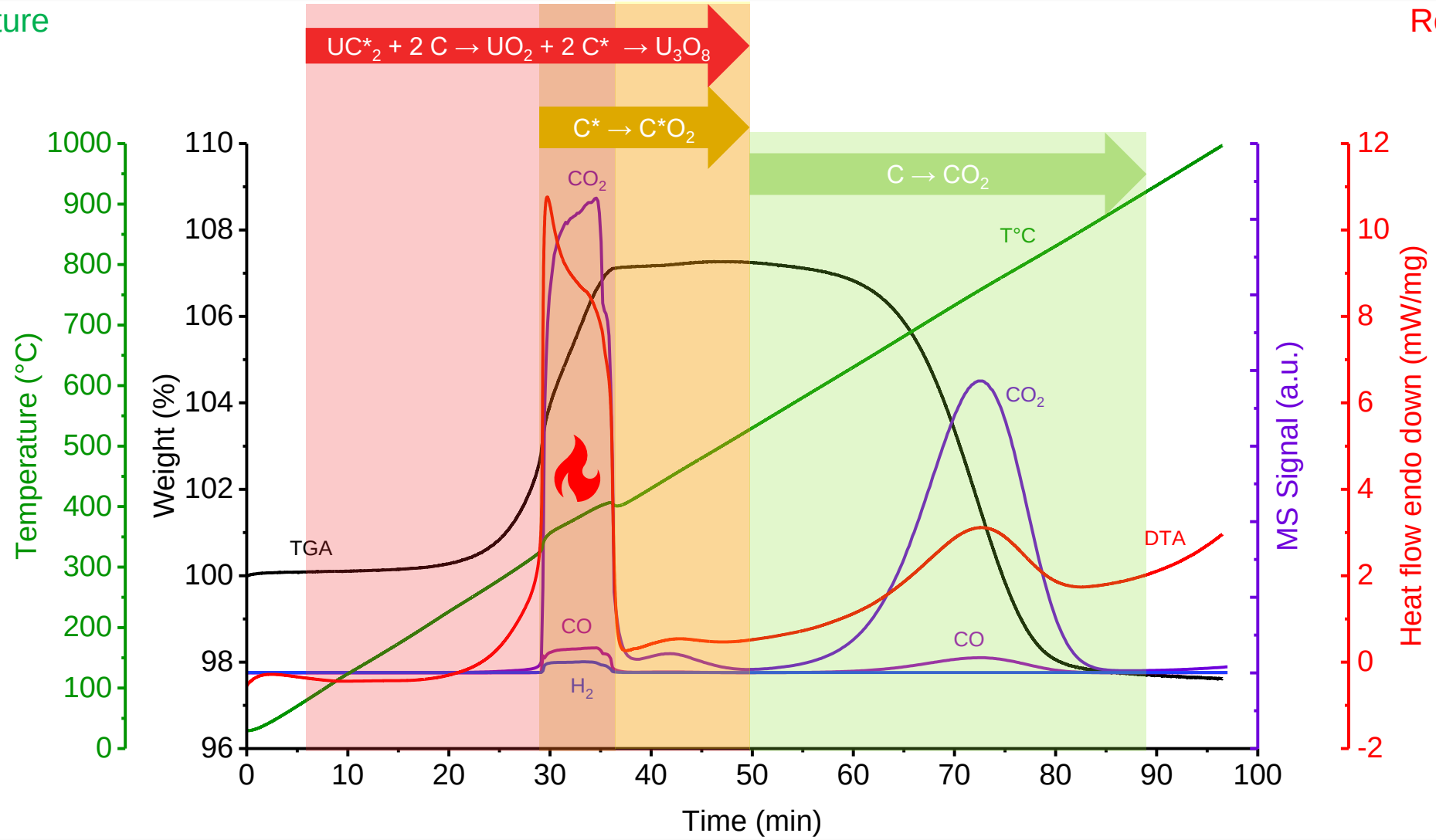
Sample Temperature
Sample Mass



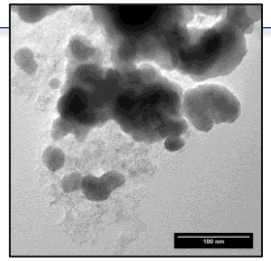
TGA-DTA-MS: UC_x oxidation pathway

Sample Temperature
Sample Mass

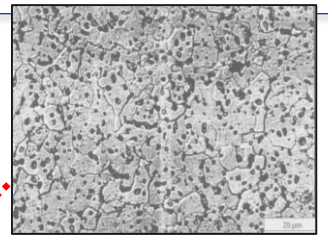
Reaction Heat flow
Gas formation



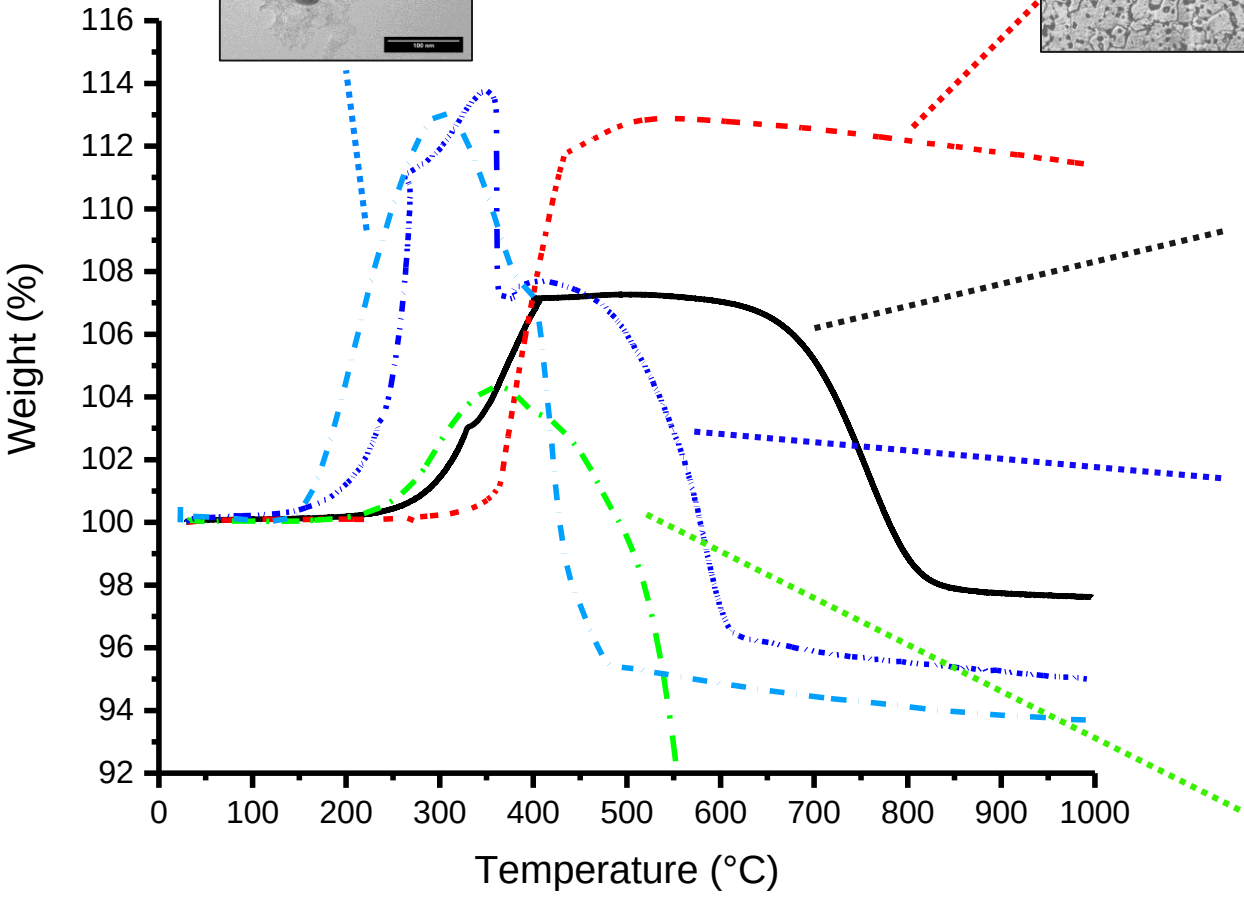
Microstructure vs Oxidation behaviour

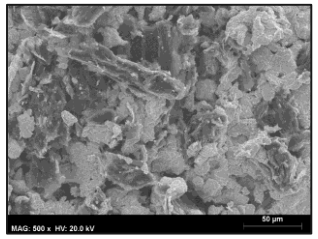


Nano UC_2
28 nm

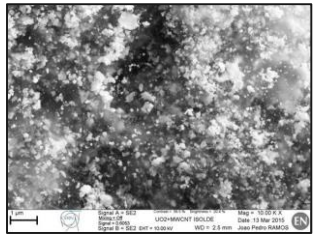


High density UC
6 µm

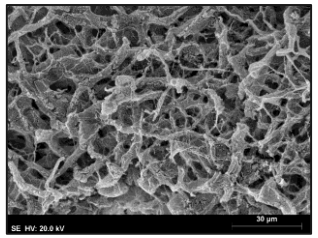




Micro UC_x
24 µm

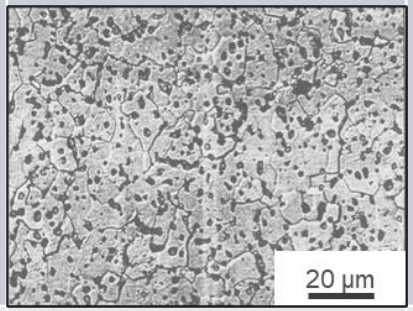
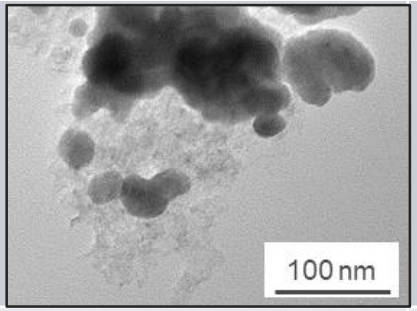
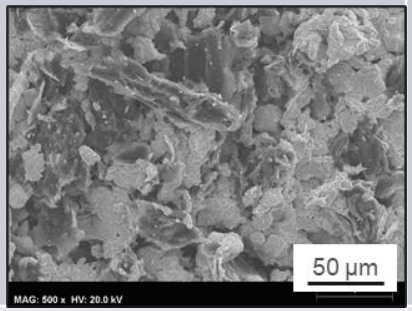
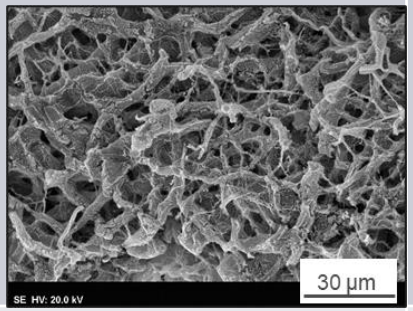
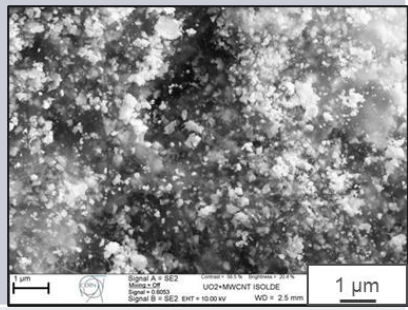


Nano UC_x
160 nm and 2 µm



Nanofibers
UC_x
4-10 nm

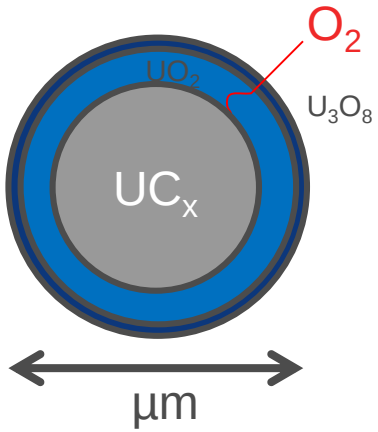
Microstructure vs onset oxidation temperatures and kinetics

Material Kinetics data	High Density UC	Nano UC_2	Micro UC_x	Nanofibrous UC_x	Nano UC_x
SEM/TEM					
Particle size	6 ± 3 µm	27 ± 8 nm	20-50 µm	4-10 nm (UC_2)	~160 nm and 2 µm
UC/UC_2 oxidation T [°C]	280	160	215	155	150
C* oxidation T [°C]	360	305	375	350	360
C_{free} oxidation T [°C]	-	-	550	410	400
Reaction model	Diffusion (D3)	2nd-order (F2)	Diffusion (VC)	Diffusion (D3)	Diffusion (D3)
Activation energy E_a [kJ/mol]	123.6 ± 4.0	88.1 ± 11.9	128.6 ± 1.7	109.4 ± 28.3	78.9 ± 7.1
Frequency factor, ln A	16.6 ± 0.8	20.8 ± 3.2	19.1 ± 0.4	19.0 ± 6.0	12.4 ± 1.9

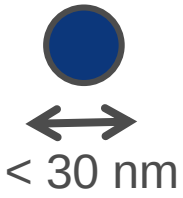
Summary of results

Micro- grain size

Mechanism:
Diffusion limited

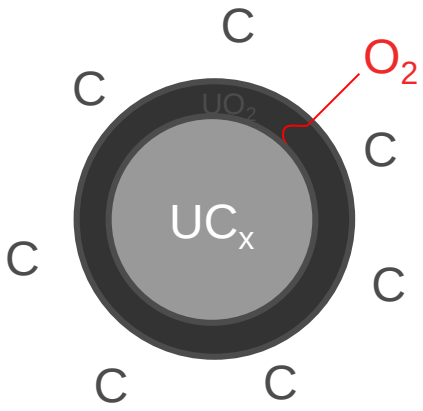


Nano- grain size



Mechanism: Surface limited (< 30 nm)
Lower onset oxidation temperature
Lower activation energy

Excess carbon



Extra passivation layer
Higher activation energy

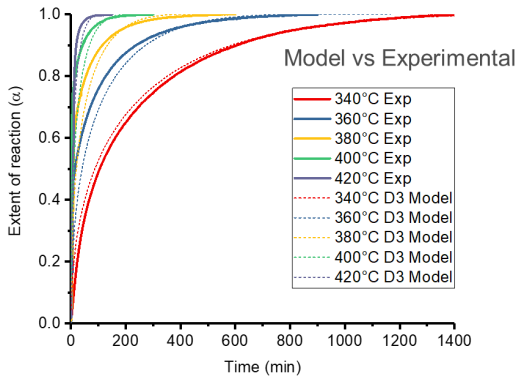
Released carbon

$$UC_2 + O_2 \rightarrow UO_2 + 2\,C$$

$$C + O_2 \rightarrow CO_2$$

Onset oxidation temperature, ~365°C, poorly dependent on starting microstructure

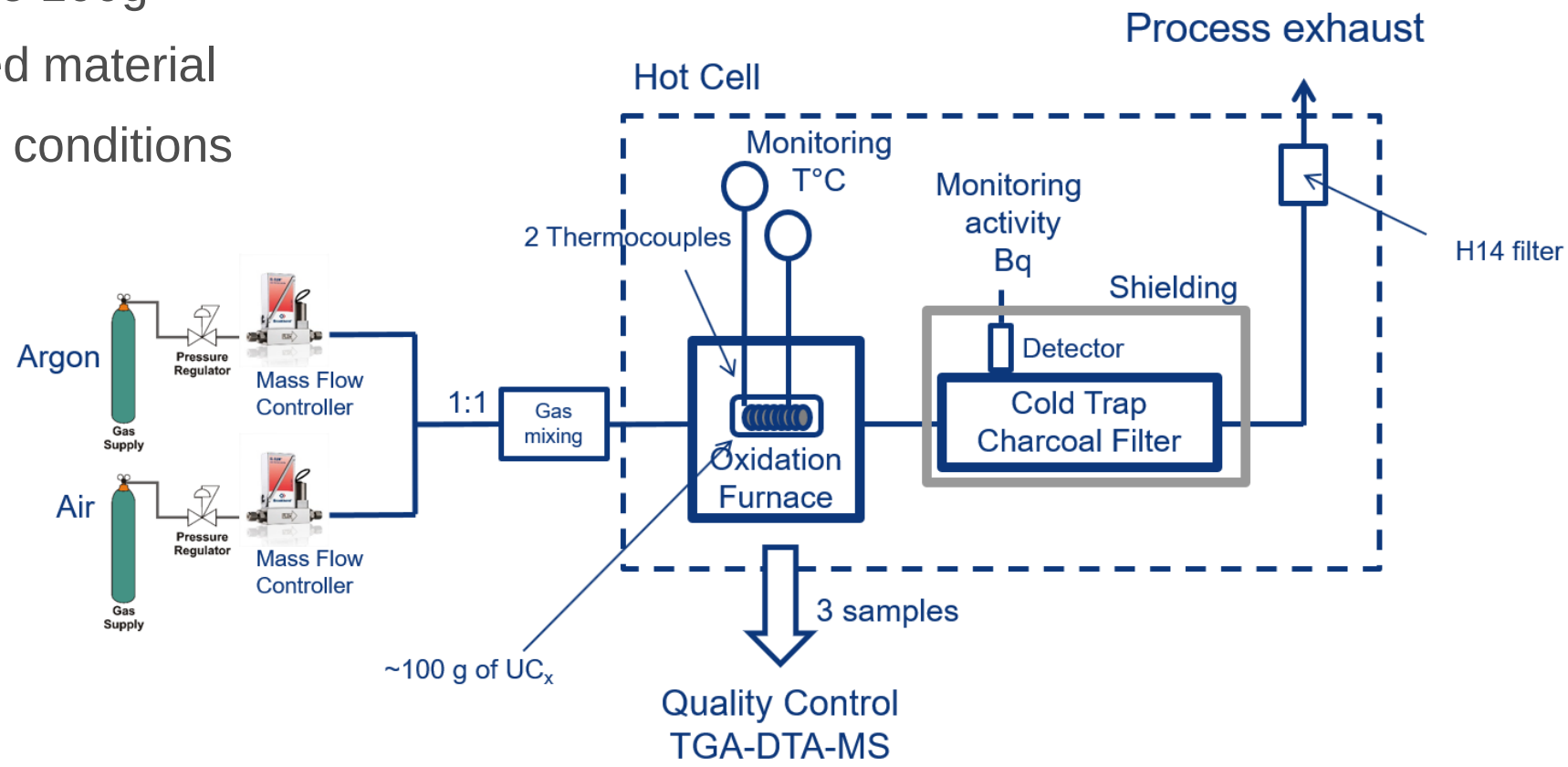
Satisfactory prediction



Application to UC_x waste disposal

Next steps:

- Scale-up studies from mg to 100g
- Repeat studies on irradiated material
- Definition of safe operation conditions



Acknowledgement

CERN
A.-P. Bernardes
T. Stora
R. Catherall
J. Vollaire
S. Rothe
B. Crépieux
M. Owen
H. Barbero
A. Vieitez Suarez
P. Harwood
B. Conde Fernandes
V. Barozier
C. Duchemin
J. Ballof
L.-P. De Menezes
P. Bertreix
A. Dorsival
E. Aubert
M. Deschamps
F. Pozzi
J. Gulley
L. Ulrici
P. Pisano
A. Broche
J.-M. Vuaillat
S. Acera
S. De Man
A. Baris

EPFL
K. Sivula
P. Schouwink
K. Agrawal

IST Lisboa - C2TN
S. Chowdhury
A. P. Gonçalves
A. Perreira
J. Branco
H. Casimiro
L. M. Ferreira
I. Dias Nogueira

SCK.CEN
J. P. Ramos

MEDICIS-Promed students

TRIUMF
A. Gottberg

Paul Scherrer Institut
D. Gavillet
H. F. Beer
A. Wällisch
P. Zimmerman

JRC-Karlsruhe
K. Popa
O. Walter
O. Dieste-Blanco
H. Hein
D. Bouexiere
T. Gouder
R. Eloirdi
R. Caciuffo
J. Y Colle

This research project has been supported by a Marie Skłodowska-Curie Innovative Training Network Fellowship of the European Commission's Horizon 2020 Programme under contract number 642889 MEDICIS-PROMED and the MEDICIS Collaboration

Thank you for
your attention!