Thick solid targets for the production and online release of radioisotopes: the importance of the material characteristics
Structure

• ISOL Method
• Target microstructure and limitations
• Facilities around the world (non exhaustive)
• Latest developments in target materials
ISOL Isotope Separation OnLine

1. Production
2. Diffusion
3. Effusion
4. Ionization
5. Mass Separation
6. Transport

Beam Int. =
ε =

Radioisotopes have finite half-lives!

N_t – Nr of exposed atoms [dim]
j – Proton flux [cm^{-2}]
σ – Cross section [mb]
ε – Efficiency [%]

Proton Transfer line
Ion Source

Extraction electrode

Target heating (1 – 2kW), <~10% beam power

4. Ionization

0.01 1 100
0.01% 1.00% 10.00% 100.00%

Radioisotopes have finite half-lives!
(Future) ISOL facilities around the world

Power! Unlimited power!!

 Beam Int. = \( \sigma \cdot j \cdot N_t \cdot \varepsilon \)

\( \sigma \) – cross section – energy/particle/target

\( j \) – flux – power – beam current

\( N_t \) – target density

\( \varepsilon \) – extraction efficiency

50 MeV e\(^{-}\) – 10 \( \mu \)A
500 W

1.4 GeV – 2 \( \mu \)A
2.8 kW (1.2 GW)

500 MeV – 100 \( \mu \)A
50 kW

40 MeV – 5 mA
200 kW

70 MeV – 140 \( \mu \)A
10 kW

600 MeV – 100 \( \mu \)A
60 kW

35 MeV e\(^{-}\) – 2.8 mA
100 kW

40 MeV – 200 \( \mu \)A
8 kW

More primary beam! \( \rightarrow \) More yield!

Reaching limits of technology to cool the targets!

More efficient TISS
New technologies \( \rightarrow \) More yield!

non exhaustive…
Target material influence on beam intensity?

Expected beam intensity vs. Target Temperature

Arrhenius dependence of effusion and diffusion with temperature

However during operation:

Targets are traditionally operated at very high temperatures (close to the materials melting point)

Arrhenius dependence of effusion and diffusion with temperature

Or even low from the beginning

Target material degradation

Melting/Sublimation
Sintering

Grain size increase
Reduction of porosity

31Ar (15.1 ms)
32Ar (98 ms)
35Ar (1.78 s)
Target material influence on beam intensity?

In most cases $\varepsilon_{\text{diff}}\varepsilon_{\text{eff}}$ limit by far the yields.

$\varepsilon_{\text{diff}} = \frac{3}{\pi \sqrt{\lambda}}$, $\mu = \frac{\pi^2 D}{r^2}$

$\lambda \leq 2\mu$

Diffusion limited release:

Assess microstructure stability

Operation $T$ ↔ Grain size/Porosity

Diffusivity (rate of diffusion) ↔ Diffusion lengths

Nano materials sinter faster
- Reduce operation temperature to stabilize

Can we stabilize porous nanostructures at high temperatures?
- Not found in the literature
- Needed R&D

Porous nanomaterials campaign started
- ~10 years ago (ISOLDE is 50 years old)
  - Shorter diffusion lengths
  - Higher porosity

- 1s – 50%
- 2s – 25%
- 3s – 12.5%
- 4s – 6.25%

Diffusion/Effusion

$\xi_{\text{diff}}x10$

$\xi_{\text{eff}}$

$\xi_{\text{t1/2}}$ = 1s

Target Temperature

10x smaller!

1μm

Same $T$!
What is sintering?

Sintering temperature (densify):
- Defined in function of the material melting point ($T_m$)

<table>
<thead>
<tr>
<th>Material Type</th>
<th>Temperature Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micrometric materials</td>
<td>0.5 to 0.8$T_m$</td>
</tr>
<tr>
<td>Nanomaterials</td>
<td>0.2 to 0.4$T_m$</td>
</tr>
</tbody>
</table>

The smaller the particle size (larger surface area) the **higher** the sintering driving force.

Main reason why nanomaterials were discarded in the past for ISOL target application.

Sintering can be affected by irradiation (defect creation).
What about the material microstructure?

As Feynman said: “There is plenty of room at the bottom”!
Impossible to go into detail in all! Please refer to the publications, talks and posters or the authors themselves for more info! Or let’s discuss during the coffee breaks!
Developing (nano)materials

Acquired and tested

2010

*submicron

CaO – J.P. Ramos, et al.

Identifying suitable target nucleus and chemical compound

Microstructure stabilization

UC$_2$ + 2C – A. Gottberg, et al.

Dec. 2012

Stabilizing microstructure at high temperature and high-power irradiation

Nov. 2014

TiC+CB – J.P. Ramos, et al.

2014

Studying diffusion and release properties

Post-irradiation material analysis

2-5 years per material

Synthesis

LaC$_2$ + 2C – J. Guillot, et al.

Nov. 2014

Reacting sintering and microstructure stabilization

2015

MWCNT – C. Seiffert, et al.

Stabilizing microstructure at high temperature and high-power irradiation

See poster of S. Rothe on ISOLDE infrastructure for material production tomorrow at 4:45 p.m.

CaO – J.P. Ramos, et al.

Dec. 2012

See poster from T. Stora on 100Sn production today at 5:30 p.m.

SiC – S. Fernandes, et al.

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Nanometric TiC – microstructure stabilization

1800 °C

TiC
(80 – 120 nm)

Graphite
(~16 µm)

Carbon Black
(~40 nm)

C Nanotubes
(~10 nm x 1.5 µm)

50 vol.% Graphite

50 vol.% C Black

75 vol.% CNT

TiC milled

1800 °C

7.7 m² g⁻¹

16.7 m² g⁻¹

12.0 m² g⁻¹

0.1 m² g⁻¹

Carbon very successfully hinders the sintering of TiC

Target materials oriented to molecular beams

Melting point 2070 °C
Reacts with other elements to form refractory compounds

Injection of CF$_4$ or SF$_6$
Formation of BF$_x$

Specific Surface Area
293.1 m$^2$/g
14.85 g of MWCNT
Area 7140 m$^2$ (68 x 105 m) – FIFA recommendation

See talk of J. Ballof today at 3:10 p.m.
Incorporation of NP SiC into PAN using electrospinning

- Jet of charged particles is emitted above a threshold voltage
- Taking advantage of the emission of sturdy fluid jet
- Separating & Immobilizing np-SiC into electrospun nanofibers

STEM/EDS-Mapping Images

Heat treated samples at 1600 °C under vacuum for 5 days

Online Irradiation Tests: Sept 25th to Oct 1st 2018

22Al, 23Al, 20Mg, 21Mg, 22Mg, 20Na, 21Na

J. Wong, et al.
BN for 11C production

Boron nitride (BN)

\[ ^{11}\text{B}(p,n)^{11}\text{C} \]
\[ ^{14}\text{N}(p,\alpha)^{11}\text{C} \]

15 MeV p

Need 4E8 ions/spill (patient)

After post acceleration

Spark plasma sintering
- 1700 °C final sintering T
- \( \rho_{\text{bulk}} = 1.3(1) \text{ g cm}^{-3} \)
- 40% porosity

BN is known to decompose at T>1000 °C

Release tests to be conducted at ISOLDE very soon!

S. Stegemann, et al.

Modest dissociation kinetics, even at 1500 °C

Release 11C as CO molecule

See talk on Thursday (20/09) at 3 p.m.
Graphene on Ta

Pristine

Production of refractory beams

Graphene (barrier properties):
- Reduced particle interactions
- Protect against oxidation
- Avoid re-diffusion

- Graphene protective up to 300 °C
- TaC protective above 650 °C

See talk of J. Ballof today at 3:10 p.m.

M. Nazarova, et al., Carbon 139 (2018) 29-34
https://doi.org/10.1016/j.carbon.2018.06.027
J. Ballof, et al., to be published
SPES targets by additive manufacturing

Activity performed @ UNIPD-DII under the supervision of Prof. P. Colombo and Dr. G. Franchin

Titanium carbide: printing and TT @ 1800 °C

Titanium carbide: first samples (2017)

S. Corradetti, et al.
TaC for Tb production

**Two synthesis routes under investigation**

**Spark Plasma Sintering** of TaC powder
- 38vol% porosity was obtained
- Pore loss noticed at elevated temperature ($T > 1600^\circ$C)
- Addition of graphite for pore stabilisation

As produced, Spark Plasma Sintering TaC + graphite (38 vol% porosity)

Porosity maintained after heat treatment @1775°C x 30 min

**Thermal de-alumination** of Ta$_4$AlC$_3$ MAX phase
- Porous Ta$_4$C$_3$ produced by heat treatment of compacted Ta$_4$AlC$_3$ powder
- Applicable to Ta$_2$AlC and to Ti$_2$AlC to produce microporous TiC$_x$

Starting Ta$_4$AlC$_3$ MAX phase

After Heat Treatment with decomposition and evaporation of Al

Characterization: thermal conductivity, phase composition, microstructure, porosity, carbon analysis
Increasing porosity using sacrificial fillers

Gas permeability: a tool to characterize SPES porous targets

<table>
<thead>
<tr>
<th>Fiber Type</th>
<th>$K_t$ $(10^{-14} \text{m}^2)$</th>
<th>$f_r$ (vol%)</th>
<th>Total Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP fibers</td>
<td>6.5</td>
<td>24.8</td>
<td>51.7</td>
</tr>
<tr>
<td>Nylon fibers</td>
<td>5.3</td>
<td>21.5</td>
<td>55.3</td>
</tr>
<tr>
<td>PMMA</td>
<td>9.4</td>
<td>60.6</td>
<td>74.0</td>
</tr>
</tbody>
</table>

Fibers allow to obtain similar permeability but with lower vol% of filler (lower total porosity) with respect to PMMA microspheres.

Experiments done at low T (up to 450 °C) and high pressure (P>1 atm), while targets are in a different regime (T ~ 2000 °C, P < 1E-2 Pa).
**Diffusion/Effusion Ar in graphite**

Graphite density = 1.8 g.cm\(^{-3}\)
Foil thickness = 3 mm
In grain diffusion coefficient = \(4.1 \times 10^{-9}\) cm\(^2\).s\(^{-1}\)

Trend of release time of Ar isotopes from graphite target versus grain size at constant density

- **40Ar** (stable element)
- **36Ar** (1.79 s)
- **32Ar** (98 ms)
- **31Ar** (15 ms)

Higher sticking time and/or foil thickness
Low diffusion rate
High density materials

See talk of V. Kuchi today at 12:30 p.m.

See poster of P. Jardin tomorrow at 4:45 p.m.

References: V. Kuchi PhD report, to be presented by mid October 2018

HRIBF – diverse target developments

RVCF = Reticulated vitreous carbon fibers

ρ = 0.5 to 1.6 g/cm³ (difficult to reproduce)

And other developments: SiC, CeS-W, Ge (liquid), and production of Si beams from Al₂O₃ forming SiS molecules

D. Stracener, et al.
$\text{UC}_x$ material developments

- UC$_x$ oxidation
- UC$_x$ nanofibers
- UC$_x$ + graphene
- UC$_x$ release studies
- UC$_x$ production
- UC$_x$ large pellets
Uranium carbide targets are the most used at ISOLDE (>60% of beam time).

High yields in most of the isotopes!

Apparently slow release but high yields
- Effusion controlled release

Seen in all nanomaterials

Carburized to form UC$_x$ + (4-x)C

A. Gottberg, et al., to be published
UCx target production ramp up at TRIUMF

Previous target production method
1. Synthesis of UC$_2$ from UO$_2$/C
2. Casting of UC$_2$ on a graphite foil (5x10$^{-5}$ Torr)
3. Loading material in a tantalum container
4. Conditioning of target material (5x10$^{-5}$ Torr)

New production method
1. Casting UO$_2$/C on a graphite foil
2. Loading material in a graphite insert
3. Synthesis of UC$_2$ at higher pressures (1x10$^{-1}$ Torr)

- Ten-fold reduction in production time
- Material with higher porosity
- Cleaner target handling
Disposal channel for UC$_x$ target materials at ISOLDE

Microstructure vs Oxidation kinetics

Murbach et al. 1965

< 100 nm ?
< 37 μm
37-74μm
74-149 μm
149-297 μm
297-650 μm
> 650 μm

Time (min)
Mass gain %

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
UC$_2$ nano fibers

**Setup for electrospinning**

**Electrospinning** at 15-20 kV

**Step 1**

**Step 2**

Heat-treatment at 550 °C (1 °C/min) to form UO$_2$

\[ \frac{U}{C} = \frac{1}{6} \]

**Step 3**

Heat-treatment at 1800 °C to form UC$_2$

(imp. 30% of UO$_2$)

\[ \frac{U}{C} = \frac{1}{4} \]

### U-Precursor + Cellulose acetate

**S. Chowdhury, et al.**
Uranium carbide with graphene precursor

\[ \text{UO}_2 + 6\text{C} \rightarrow \text{UC}_2 + 2\text{C} + 2\text{CO}, \ T > 1000^\circ \text{C} \]

100% graphene

\[ \text{UC}_x \text{-graphene} \]

UC\(_x\) crystallite sizes:
- \(\text{UC}_x + \text{graphite}: 35\) to 75 nm
- \(\text{UC}_x + \text{graphene}: 49\) to 36 nm

Also done for LaC\(_2\), however graphene acted as sintering aid instead.


20 to 40 % increase in thermal conductivity with respect to graphite
Release from multiple UC\textsubscript{x} microstructures

“Conventional UC\textsubscript{x}”

- Fully dense UC x4 more density
- Less release

CNT= nanoUC\textsubscript{x} from ISOLDE

High release

Matches online results obtained at ISOLDE

<table>
<thead>
<tr>
<th>Sample</th>
<th>Uranium source</th>
<th>Carbon</th>
<th>C/U</th>
<th>(\text{UO}_2) milling</th>
</tr>
</thead>
<tbody>
<tr>
<td>OXA</td>
<td>IPNO oxalate, natural U</td>
<td>Graphite</td>
<td>3</td>
<td>Mixer</td>
</tr>
<tr>
<td>COMP30</td>
<td>IPNO oxalate, natural U</td>
<td>Graphite + 30 wt% of microfibres</td>
<td>4</td>
<td>Mixer</td>
</tr>
<tr>
<td>PARRNe 371</td>
<td>UO\textsubscript{2}, depleted U 0.3%</td>
<td>Graphite</td>
<td>6</td>
<td>Mixer</td>
</tr>
<tr>
<td>PARRNe 894</td>
<td>UO\textsubscript{2}, depleted U 0.25%</td>
<td>Graphite</td>
<td>6</td>
<td>Planetary</td>
</tr>
<tr>
<td>PARRNe 894BP</td>
<td>UO\textsubscript{2}, depleted U 0.25%</td>
<td>Graphite</td>
<td>6</td>
<td>Planetary</td>
</tr>
<tr>
<td>CNT</td>
<td>UO\textsubscript{2}, depleted U 0.31%</td>
<td>Graphite nanotubes</td>
<td>6</td>
<td>No</td>
</tr>
<tr>
<td>GATCHINA</td>
<td>U</td>
<td>Graphite</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>
UO2 + C – Systematic study on precursors and processing

- Uranium oxalate hydrate - U(C₂O₄)₂·6H₂O
- Uranium oxide - UO₂
- Graphite
  - As prepared
  - 12 days heat treated
- CNT
- Graphene from exfoliated graphite

**UO₂ Milling**

- Standard mixing
  - Conventional protocol
- Developing protocol

**Full characterization of several UCₓ+C microstructures and correlation between characteristics**

**Principal Component Analysis**

Multivariate statistical method

Release from multiple $\text{UC}_x$ microstructures

Principal Component Analysis
Multivariate statistical method

Best target materials have CNT.
No universal target materials:

- High porosity and small grains/aggregates – better release of Kr, Te, I and Cs – new protocol
- Very large pores: better release of Sr and Ba – conventional protocol

Release of fission products – highly correlated
Large nanoUC$_2$-C disks

50 mm ø nanoUC$_x$-C target

Before HT

After HT

No big change

Full characterization is on going

See talk by B.H. Kang on Friday at 10:10 a.m.
Thank you! Merci! Obrigado!

Comments or questions?

A **big thanks** to all the people that contributed to this review talk (mentioned during the talk) from all the institutes below!

With so much work happening, maybe it is time to have a **dedicated target materials/chemistry workshop**?

- Both high power/low power
- Topics: Synthesis, Stabilization, Characterization, Modeling, Molecular beams, etc.