INL/CON-24-81694-Revision-0

# UZrCN Synthesis via Arc Melting - A Novel Synthesis Study

November 2024

Changing the World's Energy Future

David M. Sanches

Idaho National Laboratory

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**November 2024**

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Professional Nerd

# UZrCN Formation via Arc Melting

## A Novel Synthesis Study

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COLLEGE OF ENGINEERING
MECHANICAL ENGINEERING
VIRGINIA TECH
NUCLEAR ENGINEERING

# Background – UZrCN

- Originally researched by USSR (1960s)
  - Carbothermic reduction [1]
- ↑ Thermal conductivity
- ↑ Stability under volatile high temperature gases (2800 K) [1]
- Potential uses:
  - Space nuclear propulsion [2]
  - HTGR's [3]

Table 1 – Comparison of High Temperature Ceramic Properties

| Parameter | $UO_2$ | UN | UZrCN | Reference |
|---|---|---|---|---|
| Thermal Conductivity (W/m-K) | 3 | 28 | 32 | [4] |
| Permissible Operation Temperature (K) | 2200 | 1700 | 2900 | [5] |
| Melting Point (inert medium, K) | 3100 | 3120 | 3120 | [5] |
| Uranium Content (g/cm$^3$) | 9.7 | 13.5 | 12.5 | [4] |
| Ultimate Strength (MPa) | 500 | 1950 | 1500 | [4] |

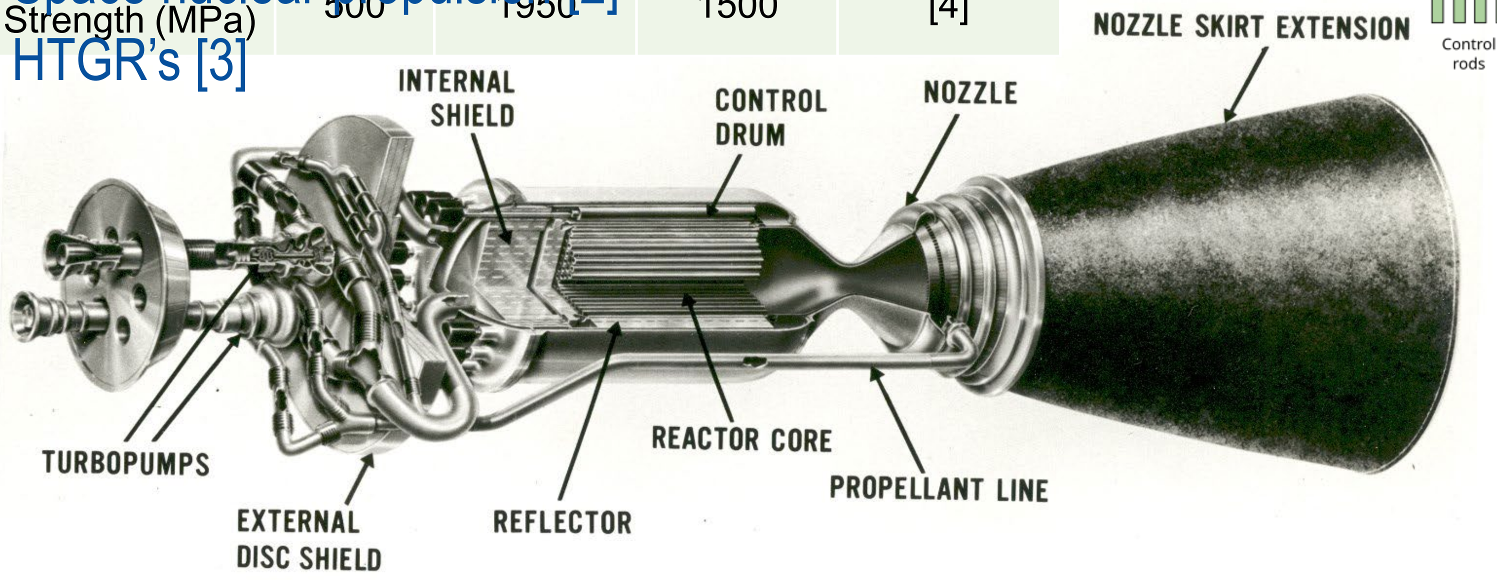


*Fig. 1 – Illustration of the NERVA nuclear thermal rocket design [Credit: NASA]*

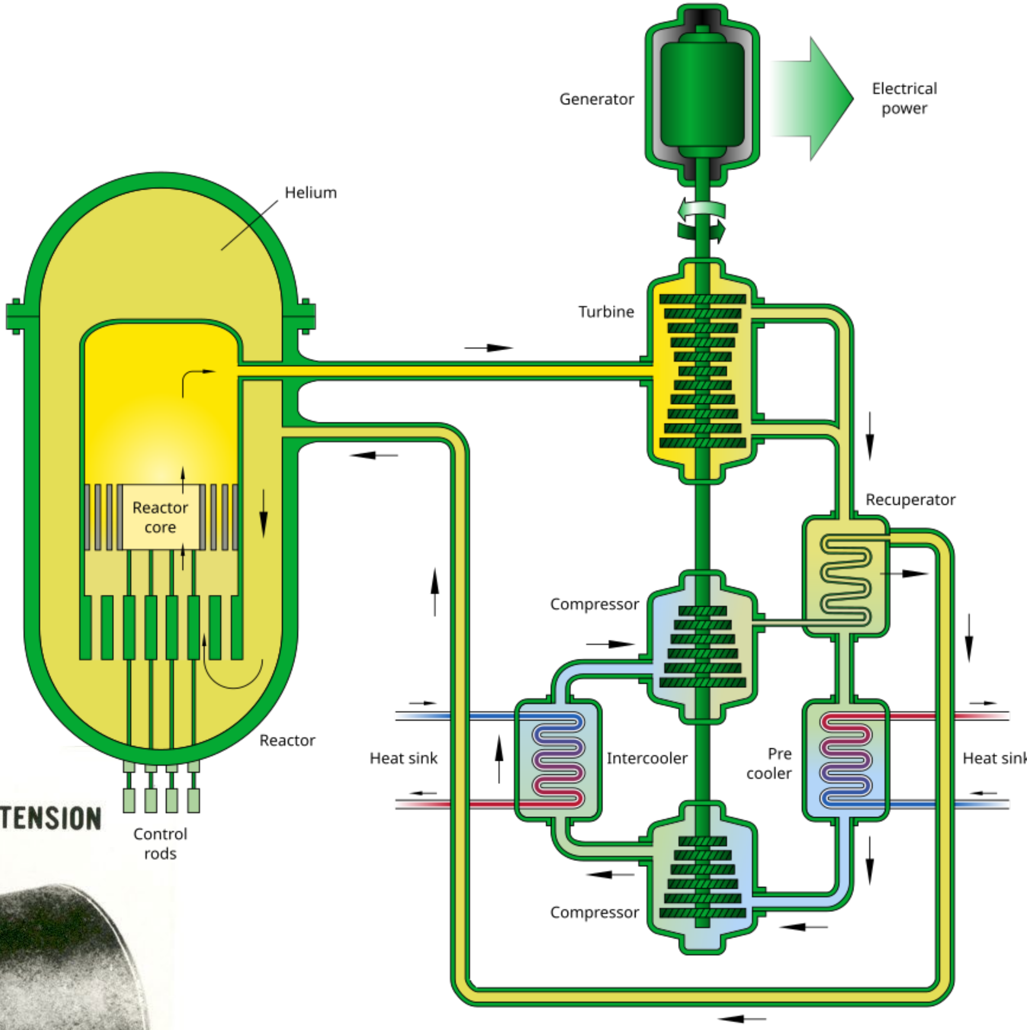


*Fig. 2 – Illustration of a High Temperature Gas Reactor design [Credit: DOE Office of Nuclear Energy]*

# UZrCN Synthesis by Arc Melting

- High temperature, liquid synthesis method
  - Proof of concept for scalable technology; induction casting
- 3 different fabrication orders investigated:
  - All methods: 300A maximum applied amperage

Table 2 – Fabrication Parameters

| Method | Target Stoichiometry | Nitrogen Flowrate | Nitrogen Pressure | Total Arc Duration (Gas) | Final Sample Mass |
|---|---|---|---|---|---|
| **1]** UZrC + N | $U_{0.5}Zr_{0.5}C_{0.5}N_{0.5}$ | 1 lpm | 0.5 psi | 190s (Argon) + 180s (Nitrogen) | 2.85g |
| **2]** UZrN + C | $U_{0.2}Zr_{0.8}C_{0.5}N_{0.5}$ | 2 lpm | 0.5 psi | 510s (Nitrogen) + 1080s (Argon) | 10.65g |
| **3]** UZr + (C + N) | $U_{0.2}Zr_{0.8}C_{0.5}N_{0.5}$ | 1 lpm | 0.5 psi | 270s (Nitrogen) | 2.48g |

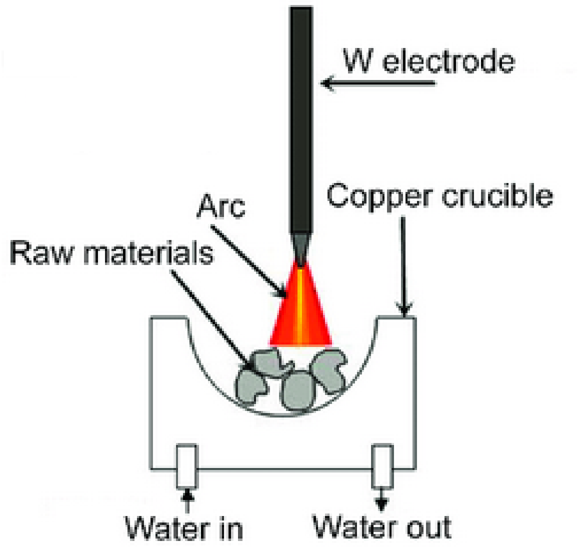


*Fig. 3 – Basic arc melt furnace schematic drawing [6]*

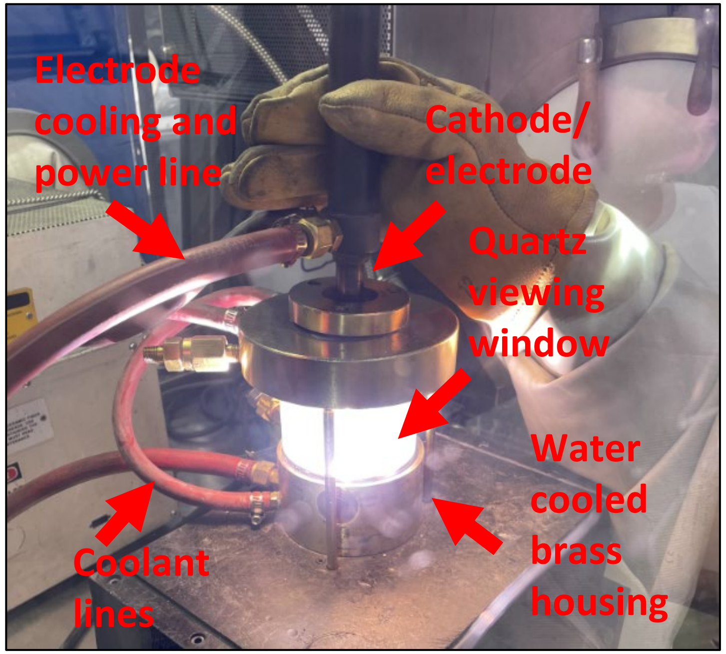


*Fig. 4 – Arc melt furnace during operation*

# UZrCN Synthesis by Arc Melting

- Initial observations:
  - Carbon sublimation
  - **Nitrogen reaction**
  - Tungsten electrode damage
    - Manipulation of amperage to avoid erosion
    - Plasma envelope widens as electrode degrades

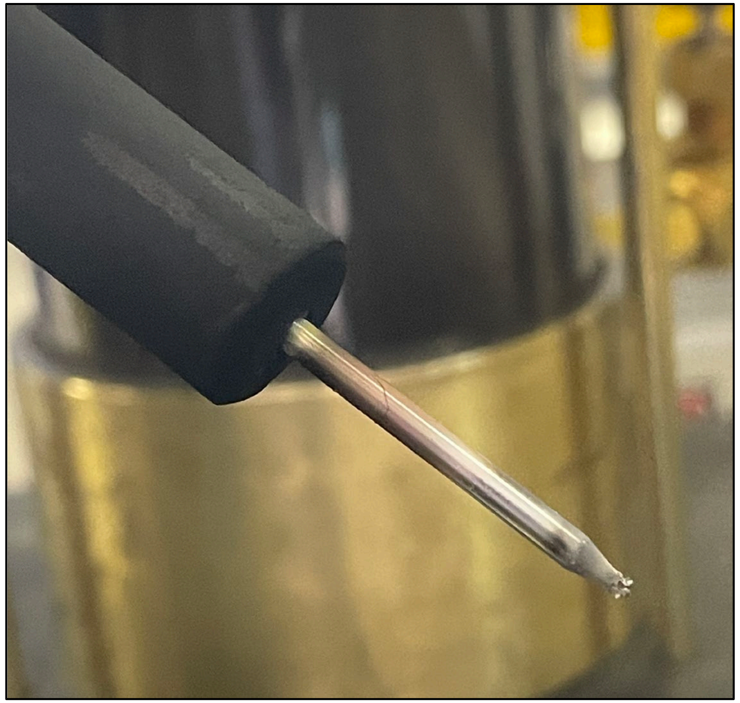

*Fig. 6 – Erosion of the tip of the tungsten electrode from high temperature reaction with nitrogen*

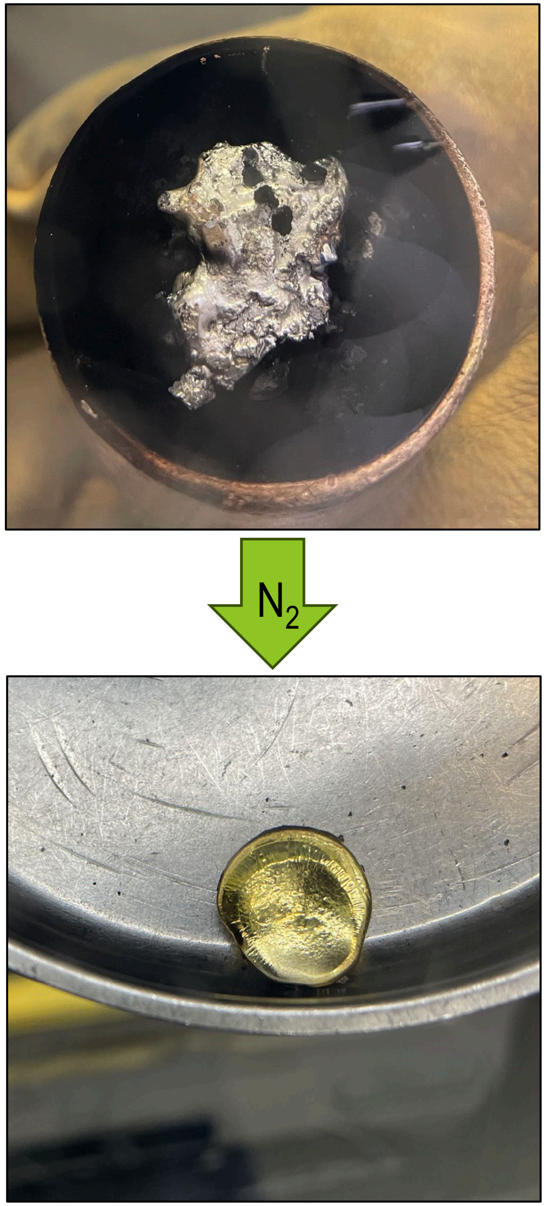


*Fig. 5 – Photograph showing golden hue after melt indicating nitrogen reaction*

# Microstructure Analysis

## Method One

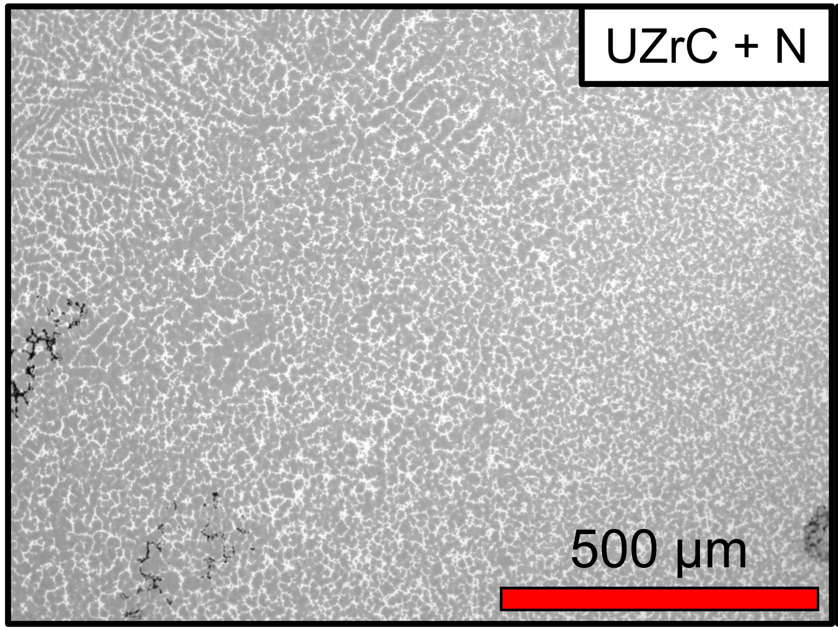


*Fig. 7 – SEM-BSE (100x) image of Method One with target stoichiometry $U_{0.5}Zr_{0.5}C_{0.5}N_{0.5}$*

## Method Two

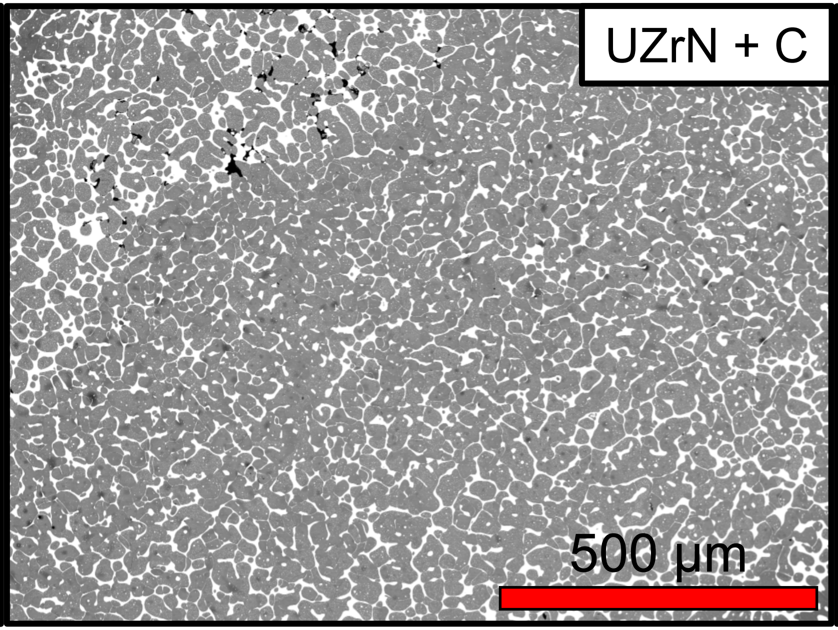


*Fig. 8 – SEM-BSE (100x) image of Method Two with target stoichiometry $U_{0.2}Zr_{0.8}C_{0.5}N_{0.5}$*

## Method Three

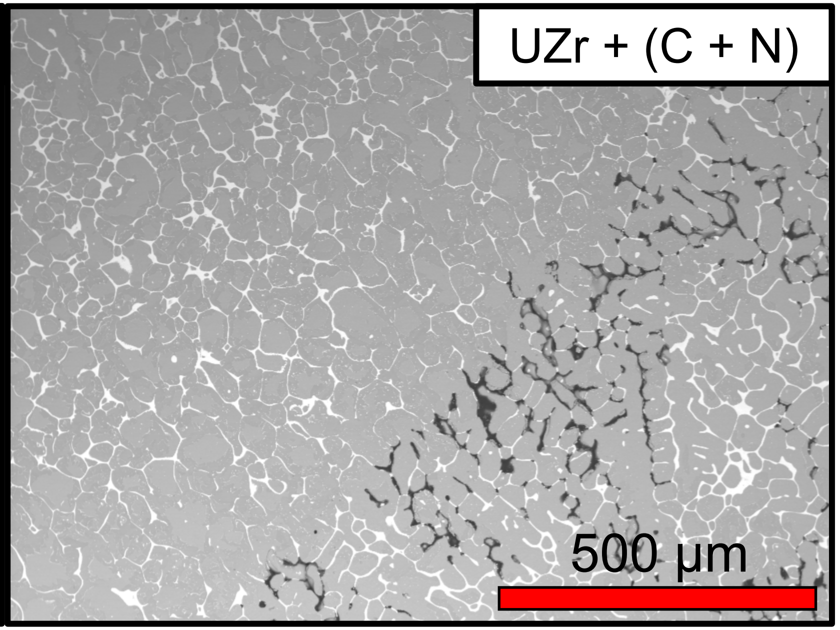


*Fig. 9 – SEM-BSE (100x) image of Method Three with target stoichiometry $U_{0.2}Zr_{0.8}C_{0.5}N_{0.5}$*

# Microstructure Analysis: Extreme Cooling Rate

- All methods exhibited two distinct microstructures as a function of the cooling rate relative to melting temperature
- Dendrite growth along crucible edges
- Segregations throughout buttons [7,8]
  - Indication of significant cooling mismatch
  - Occurs in solid solutions especially when solute melts more readily than solvent
  - Hence, uranium is rejected from solidification front into intergranular regions

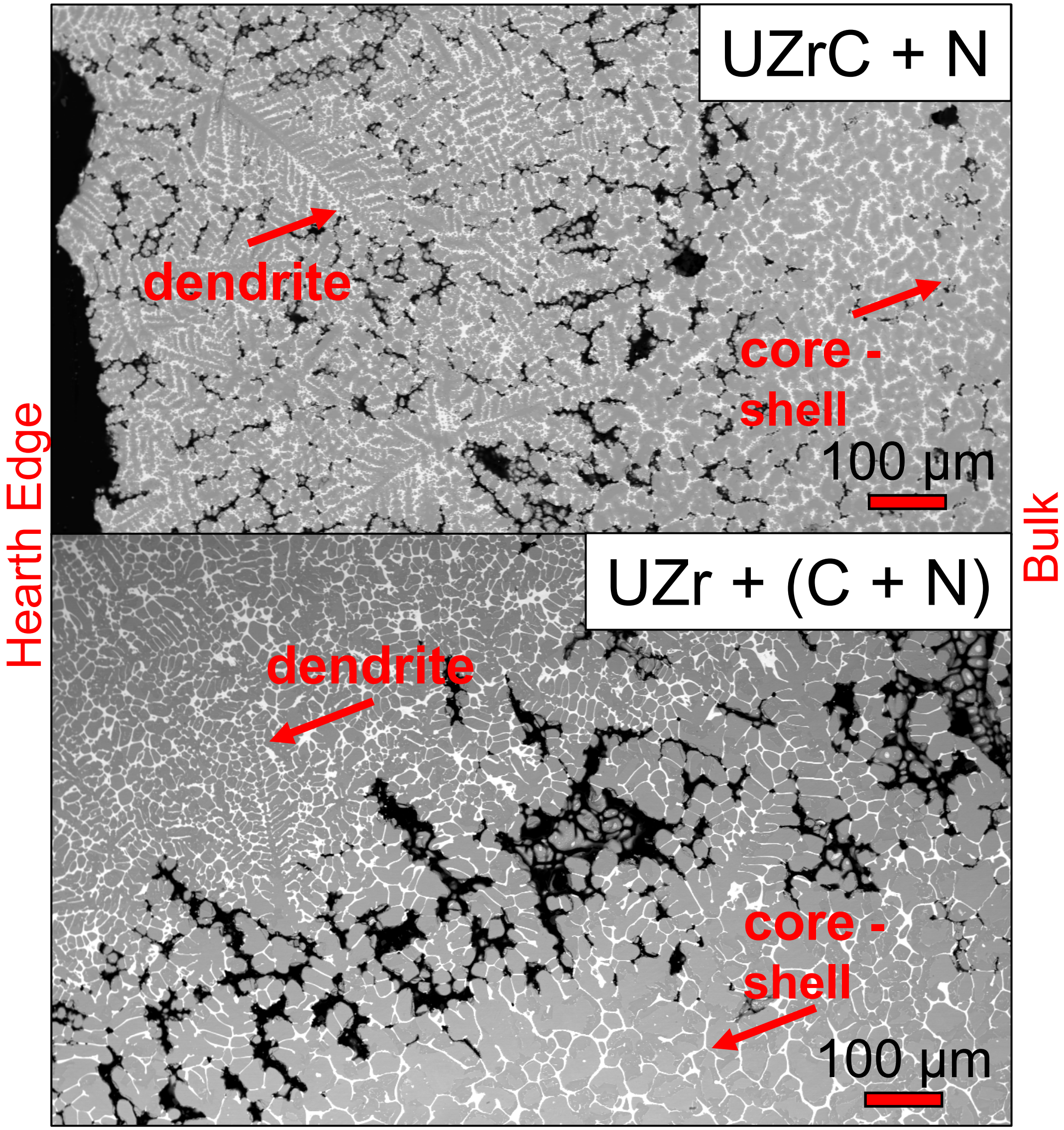


*Figure 10 - Showing SEM-BSE 100x Images of Methods 1 and 3 showing similar microstructure*

# Microstructure Analysis: Uranium, zirconium

- EDS indicates presence of uranium and zirconium
  - Uranium-zirconium interdiffusion
  - Zirconium-rich core with uranium rich shell

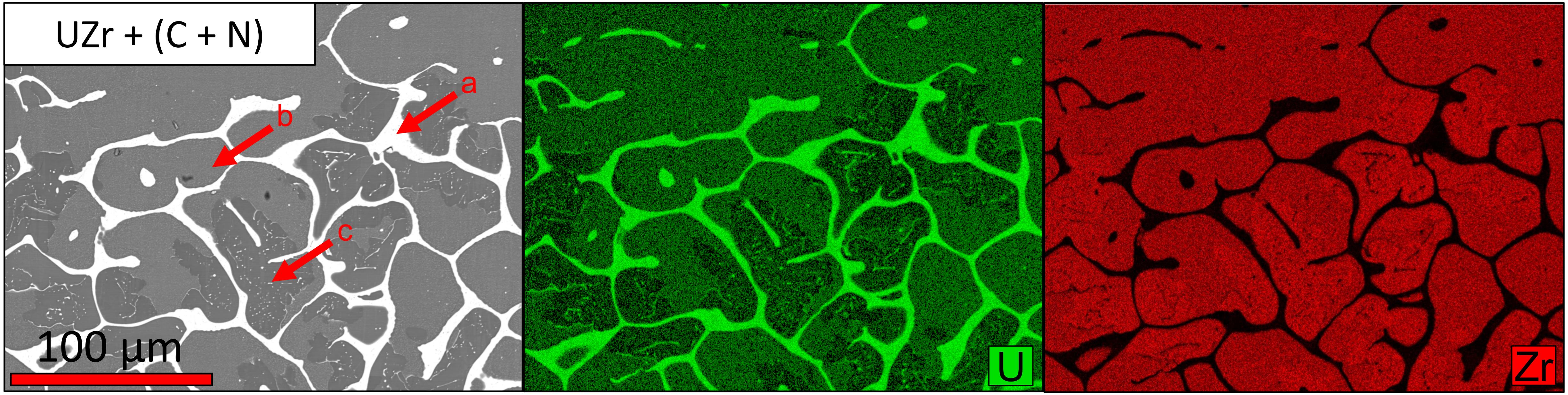


*Fig. 11 – SEM-BSE (1000x) image of Method Three with EDS maps representative of all samples (carbon and nitrogen maps excluded due to inadequate EDS resolution) Arrows point to different regions of the microstructure: a – α-uranium shell, b – zirconium-rich core with evidence of nitrogen decomposition, c – zirconium-rich core region with less decomposition effects*

# Microstructure Analysis: Nitrogen Decomposition

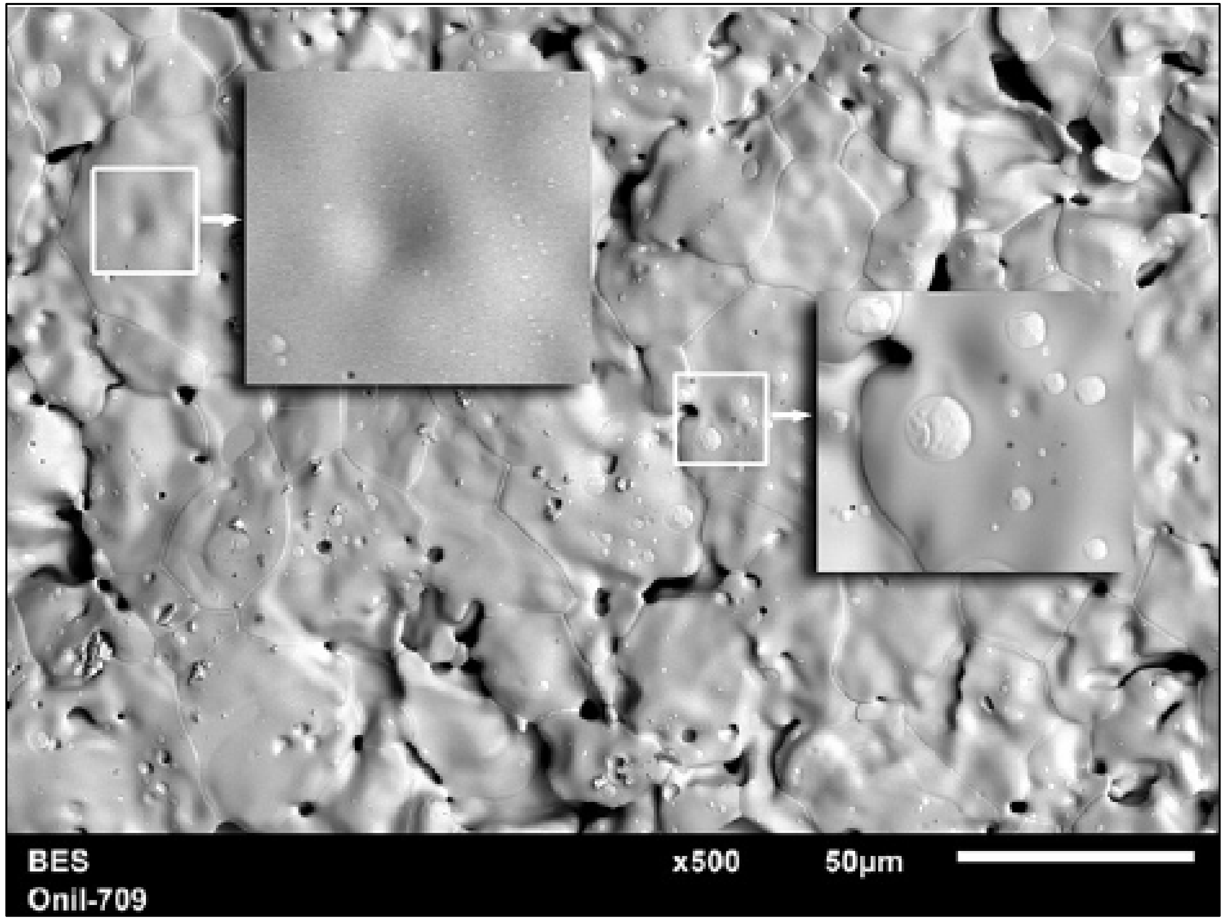

*Fig. 12 – SEM-BSE 500x image of UN thermally treated from Artem Lunev et al. [9]*

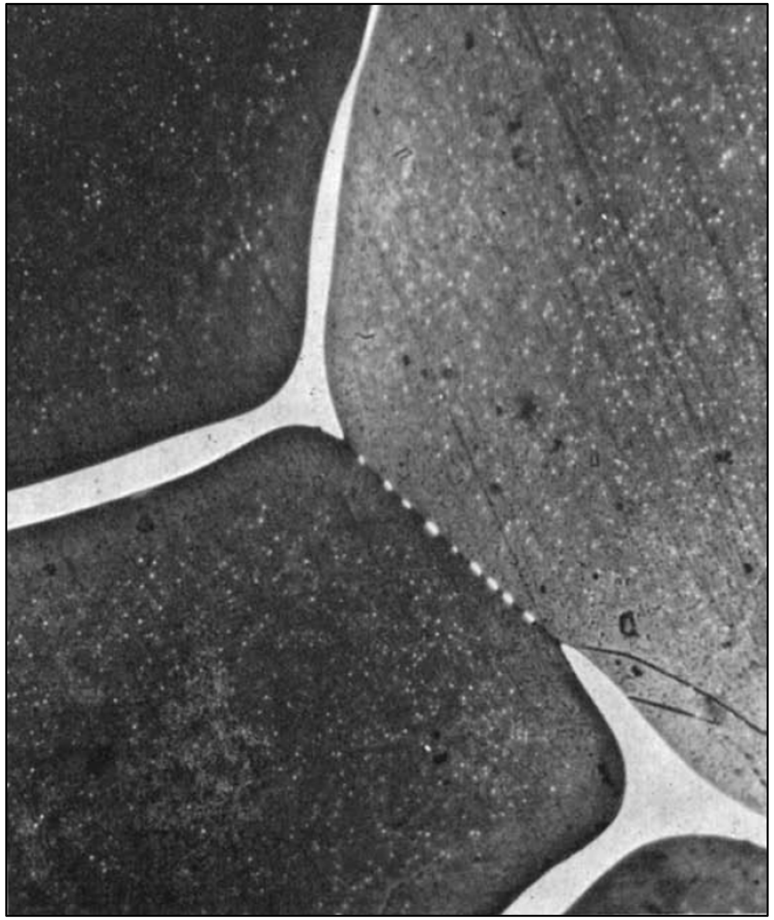
*Fig. 13 – 400x Image of arc melted UCN thermally treated from Mitsuhiro Ugajin [10]*

# Microstructure Analysis: Nitrogen Decomposition

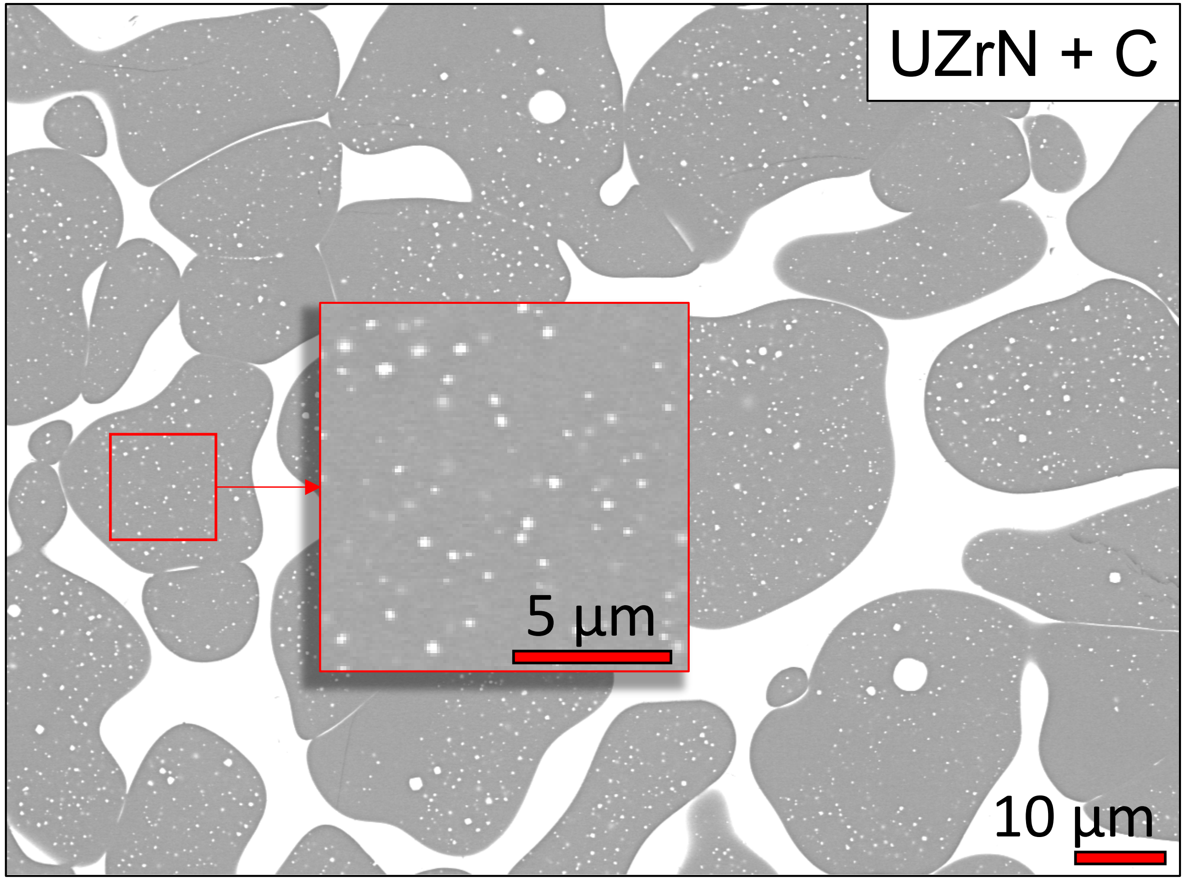


*Fig. 14 – SEM-BSE 1000x Image of Method Two*

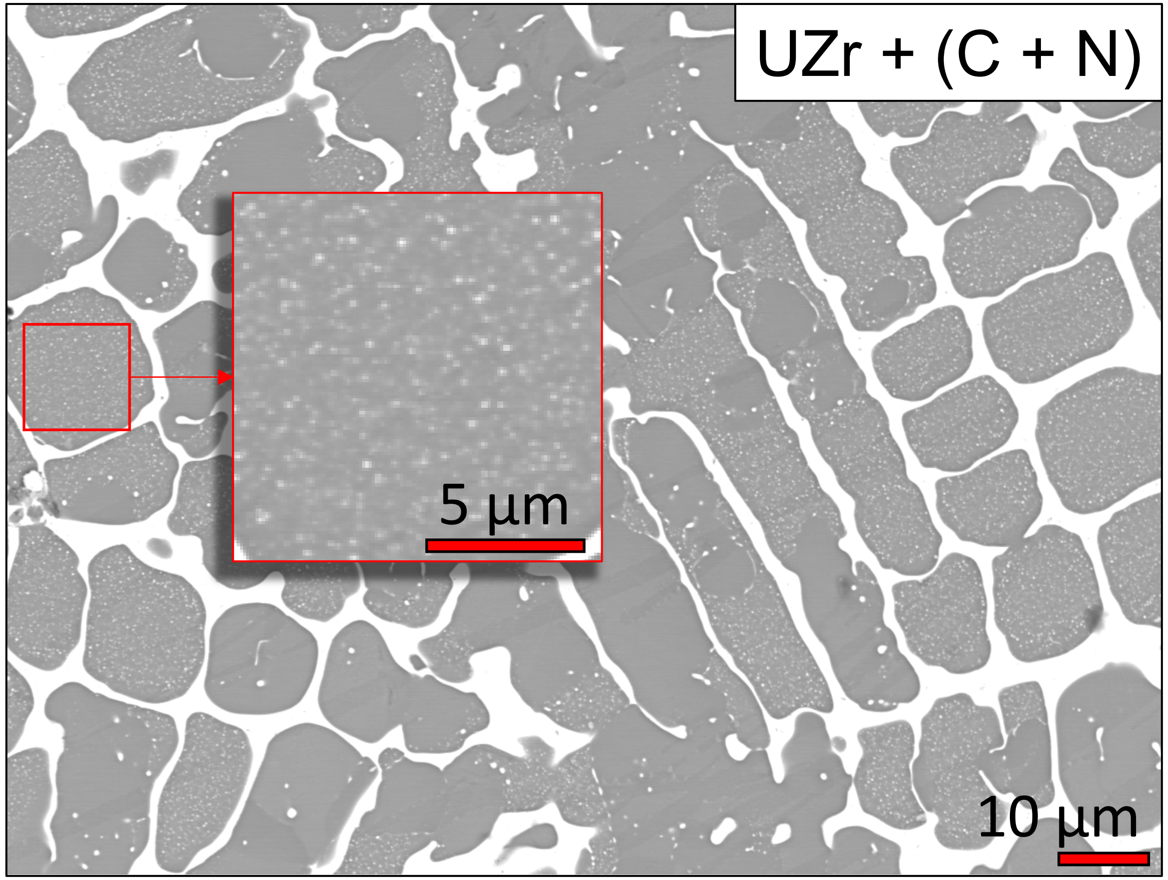


*Fig. 15 – SEM-BSE 1000x Image of Method Three*

**Precipitate formation indicates the presence then decomposition of nitrogen during the melt process!**

# XRD and LEA

- XRD shows near target phases
  - UZr vs. UZrC/N
  - LEA shows nitrogen and carbon retention
- **SEM, XRD, and LEA together indicate formation of UZrCN!**

Table 3 – Average Light Element Content

| | $\bar{N}$ wt% | $\bar{N}$ Target wt% | $\bar{C}$ wt% | $\bar{C}$ Target wt% |
|---|---|---|---|---|
| **Method 1** | 1.86 | 3.95 | 3.97 | 3.38 |
| **Method 2** | 0.89 | 5.25 | 5.10 | 4.5 |
| **Method 3** | 2.74 | 5.25 | 4.34 | 4.5 |

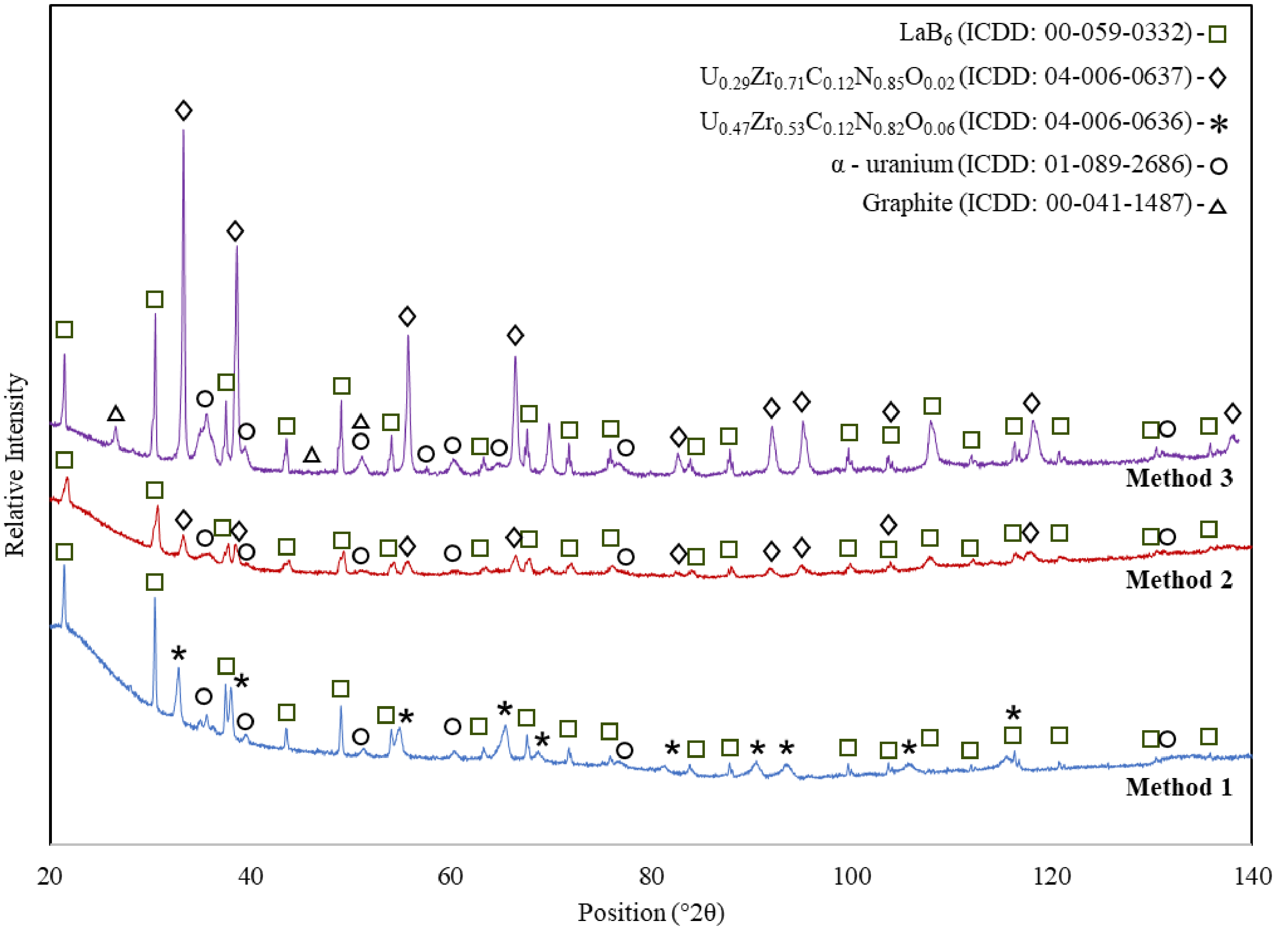


*Fig. 16 – XRD Patterns of all three methods showing UZrCN with slight oxygen contamination. $LaB_6$ Used as a reference peak [11]*

# Conclusions and Further Work

- **UZrCN can be fabricated by direct casting**
- Homogenization to be pursued
  - Tri-Arc Melt furnace
  - Nitrogen blanket in furnace
- Final stoichiometry to be evaluated
  - Atom Probe Tomography
- Process refinement toward target stoichiometry
- Extreme environment testing

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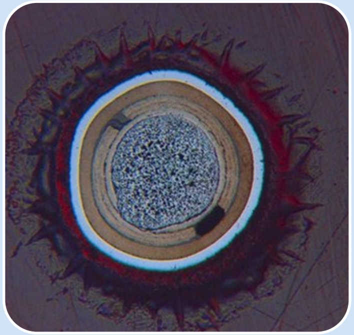
# MFC Nuclear Research, Development & Demonstration Capabilities (*with other connected INL capabilities*)

### Fabrication

- Experimental Fuel Facilities
- Fuels & Applied Science Building
- Fuel Manufacturing Facility
- Zero Power Physics Reactor
- Analytical Laboratory
- Advanced Fuels Facility



### Fresh Fuel Characterization

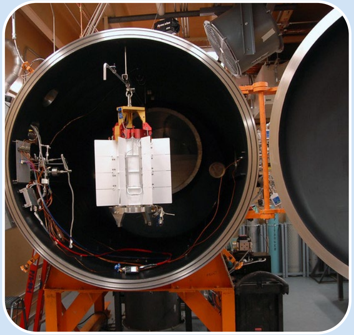
- Fuels & Applied Science Building
- Analytical Laboratory
- Experimental Fuel Facilities

### Irradiation

- Transient Reactor Experiment & Testing (TREAT)
- Neutron Radiography Reactor (NRAD)
- Advanced Test Reactor (ATR)
- Offsite Reactors

### Post-Irradiation Examination & Characterization

- Hot Fuel Examination Facility
- Irradiated Materials Characterization Lab
- Fuel Conditioning Facility
- Analytical Laboratory
- Fuels & Applied Science Building
- Electron Microscopy Lab
- Neutron Radiography Reactor (NRAD)



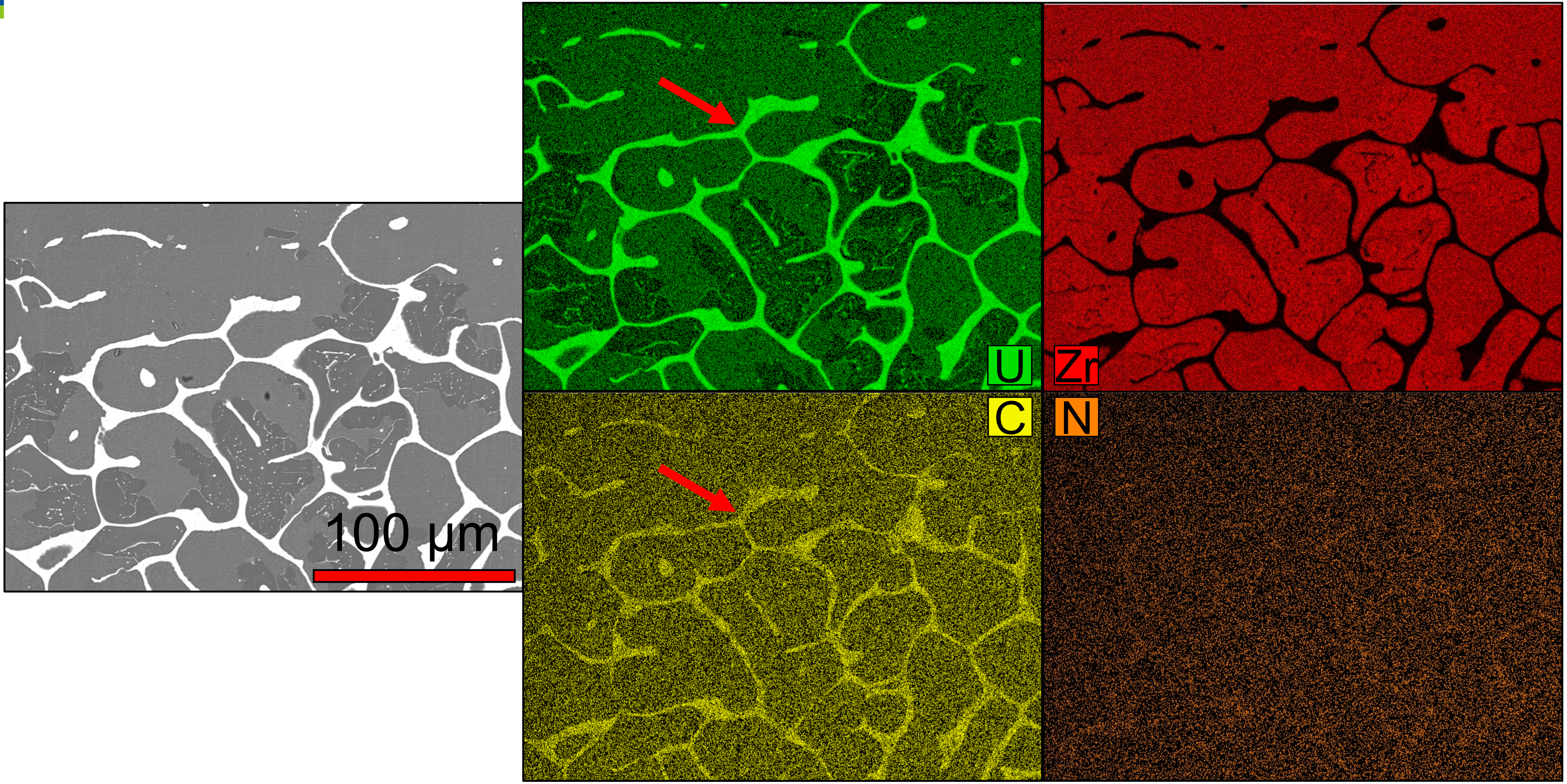
### Space Nuclear Power and Isotope Technologies

- Space & Security Power Systems Facility
- Engineering Development Lab
- Idaho Nuclear Technology & Engineering Center

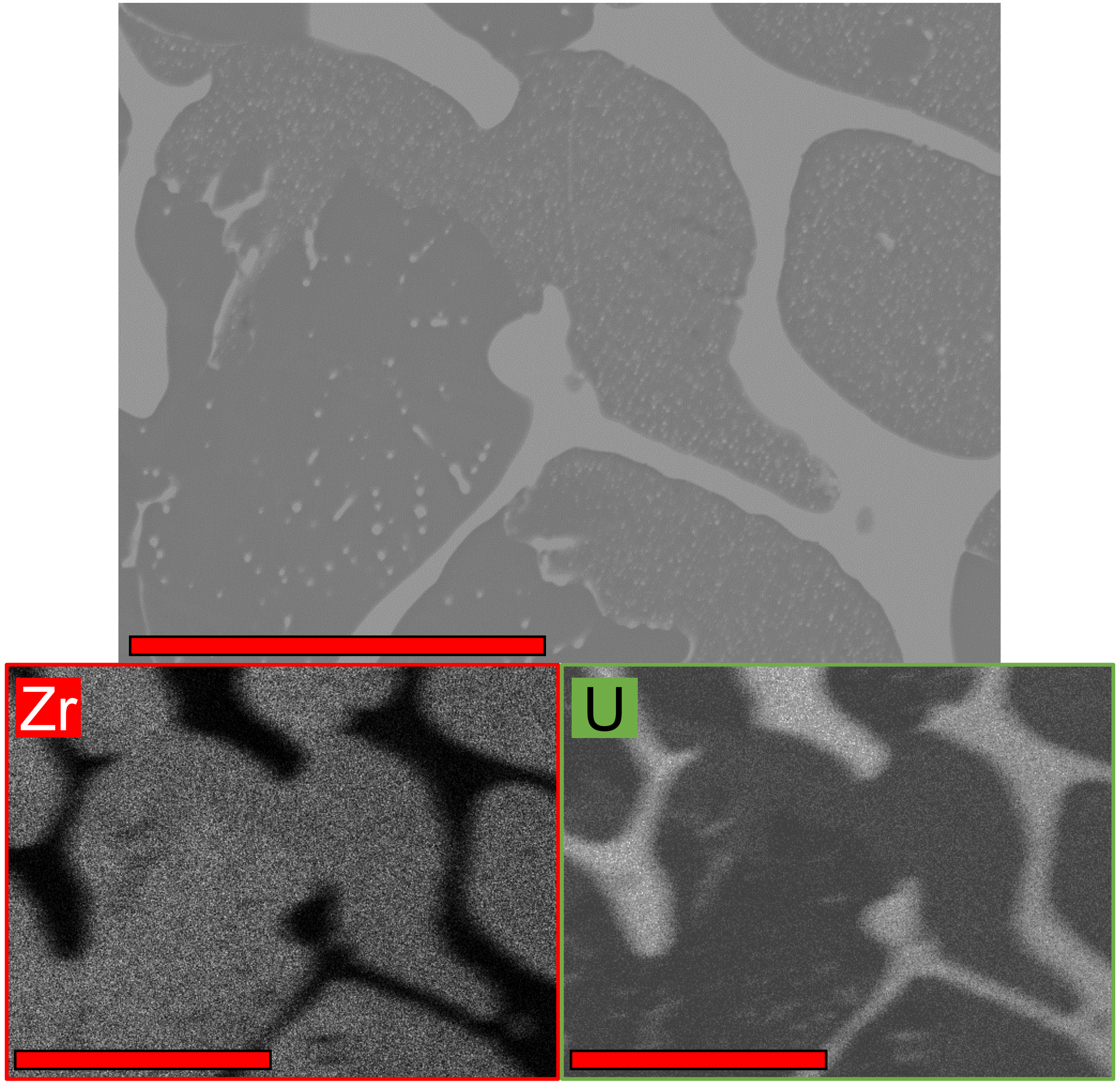
### Advanced Reactor Demonstration Test Beds

- TREAT micro-Reactor Experiment Cell
- Laboratory for Operations and Testing in the US
- Demonstration of Microreactor Experiments

# EDS Analysis: Method 3 +C/N Maps



# Wavelength Dispersive X-ray Spectroscopy (WDS)




*SEM-BSE and WDS (1500x - all scale bars 30 µm) of Method 3 with microstructure characteristic of all samples*

# Analytical Equipment

- JEOL IT-500HR Scanning Electron Microscope (SEM)
  - Oxford “Ultim Max” Energy Dispersive X-ray Spectroscope (EDS)
  - Oxford “Wave” Wavelength Dispersive X-ray Spectroscope (WDS)
- Malvern PANalytical Aries Research X-ray Diffractometer (XRD)
  - Highscore Plus for data analysis
- **ELTRA ONH-2000/CS-800**

# Pseudo Ternary Zr-ZrC-ZrN