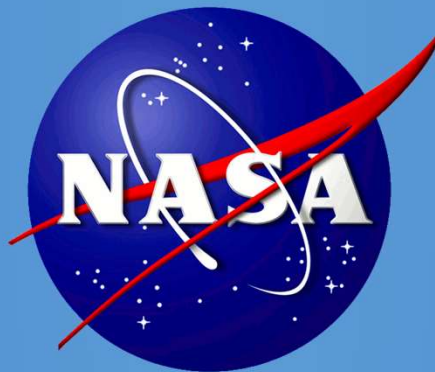


Additive Manufacture of Porous Zirconium Carbide for Nuclear Thermal Propulsion In-Core Insulators

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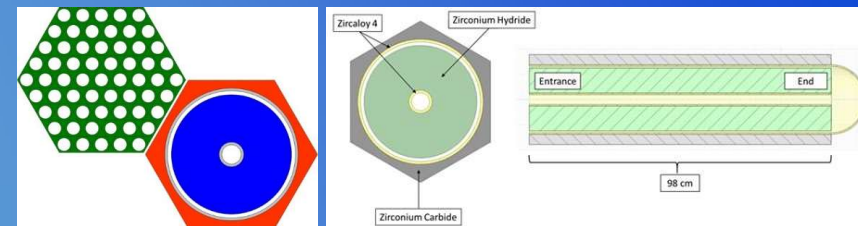
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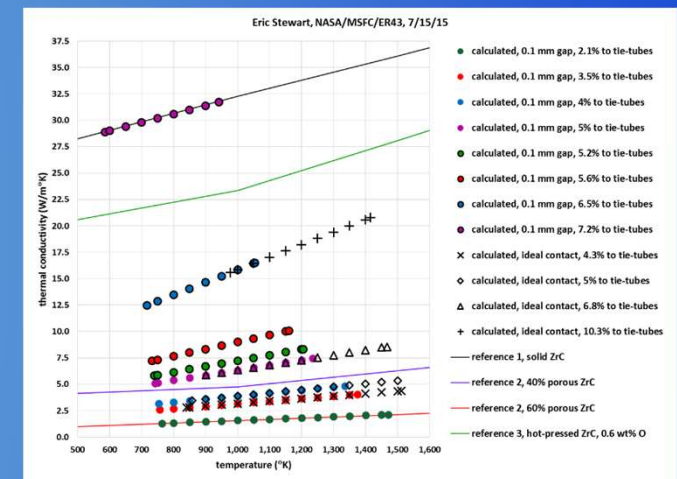
Background

- Nuclear Thermal Propulsion (NTP) in development to enable rapid-transit of long duration missions beyond low earth orbit.
- Reactor operating conditions severely limit potential material candidates for fuel, structure, moderator, insulators, etc.



NTP tie-tube sleeve insulators.

- Zirconium carbide (ZrC) is a promising candidate for NTP:
 - High melt temperature (T_m) of 3,520 °C.
 - Excellent hydrogen compatibility at elevated temperature.
 - Low neutron absorption cross section.
 - Relatively low density (ρ) of 6.73 g/cm³.
 - High compressive strength and hardness .
- Unfortunately, fully dense ZrC thermal conductivity (k) of ~ 20 W/m-K (at 20 °C) is considered a weak conductor.
- Decreasing ρ to ~ 60 percent theoretical density (%TD) decreases k to < 2.5 W/m-K and remains low with increasing temperature.



ZrC thermal conductivity vs. temp, %TD, & stoichiometry.

Problem

- Previous efforts during the ROVER-NERVA to fabricate porous ZrC investigated:

1. Powder Process

- Hot press ZrC powder mixed with a pore-former such as Teflon.
- Teflon removed by hydrogen decomposition at elevated temperature.

2. Conversion

- Compress carbon felt to shape in a die.
- Machine the felt preform to a near net shape.
- Chemical vapor infiltration (CVI) and conversion of carbon fiber into ZrC (40-110 hours).
- Grind to final shape.

- Traditional processes did show promise although they were relatively difficult, time consuming, expensive, and did not extend beyond lab scale demonstration articles.
- The ability to produce ZrC at desired ρ is not within commercial industry and the need develop a reliable supply is of importance to NTP.

Methodology

- Binder Jet Additive Manufacture (AM)

- A liquid resin binder is deposited onto a layer of powder to adhere particles together.
- A heat lamp attached to the recoater assembly dries and lightly cures the layer.
- Post-build the chamber is heated in an oven to cure the binder to form “green parts”.
- Green parts unpacked from the powder bed and undergo powder removal.
- Green parts heat treated in a furnace to burn-out polymer binder and sinter to densify “brown parts”.
- Primary disadvantage is the a low post-sintered density of ~60 %TD.

- Objectives

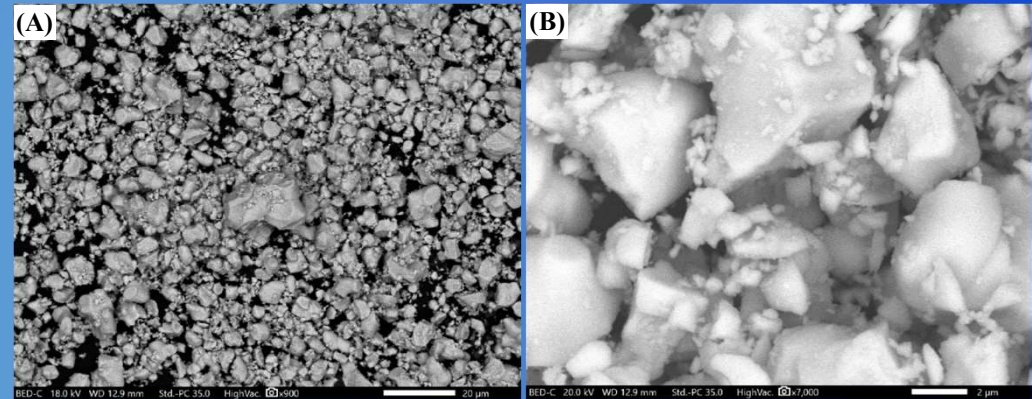
- Investigate binder jet AM and associated post-processing to yield net shape ZrC with 60 %TD with desired thermal conductivity and strength. University of Texas at El Paso (UTEP) W.M. Keck Center for 3D Innovation leveraged for binder jet AM experience.

- Tasks

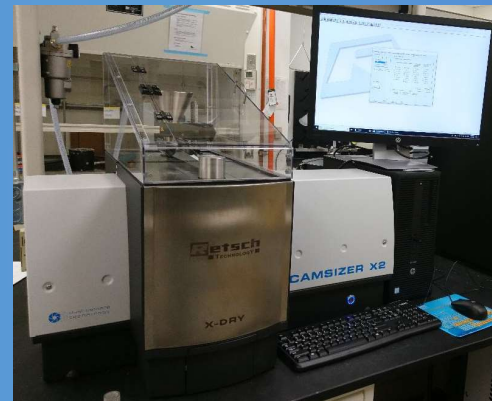
- Binding agent selection & parameter development (UTEP).
- Heat treatment to achieve 60 %TD & sub-stoichiometry (MSFC).
- Microstructure (UTEP & MSFC).
- Mechanical properties vs. %TD (MSFC).
- Thermal conductivity vs. %TD (MSFC).

Powder Characterization

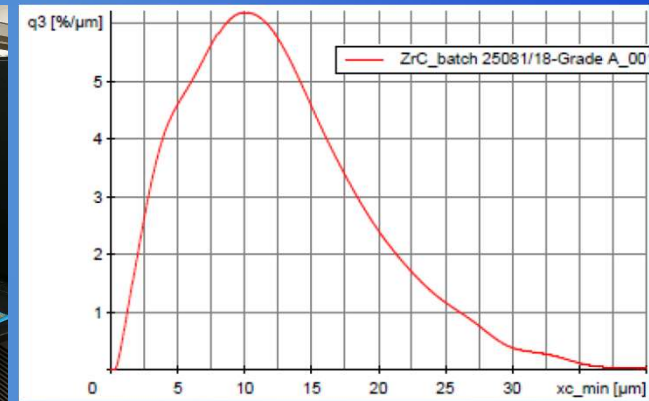
- Binder jet powder feedstock advantages:
 - Broad particle size distribution (PSD)
 - Angular morphology
 - Non-fully dense particles
 - More flexible powder requirements = lower cost
- ZrC grade AX powder obtained (H.C. Starck)
 - Maximum hafnium content 0.2 wt%.
 - Hafnium needs to be minimized due to a large neutron absorption cross section.
- Retsch Camsizer X2 to determine PSD
 - D10: 2-4 μm
 - D50: 7-12 μm
 - D90: 17-27 μm



Scanning electron micrographs of as-received ZrC powder (A) at 900x and (B) 7000x.



UTEP Retsch Camsizer X2



ZrC grade AX PSD.

Binder Jet AM Parameter Development

- ExONE Binder Jet AM Platforms
 - M-Lab: 40 x 60 x 35 mm
 - Innovent+: 160 x 65 x 65 mm
- Binding Agent Selection
 - Fluid Fuse (solvent-based) binder
- Powder Behavior
 - Flowability
 - Spreadability (uniform distribution across the build plate)
- Build Parameter Optimization Trials
 - 36 Trials
 - Al_2O_3 parameters used as start values
 - Layer thickness (10, 20, 40, 60 μm)
 - Recoater powder spread rate (1, 3, 5, 10, 15 mm/s)
 - Binder saturation (25, 60, 80, 100%)
 - Drying time (4, 5, 8, 10, 90 s)



UTEP ExONE M-lab Binder Jet AM machine



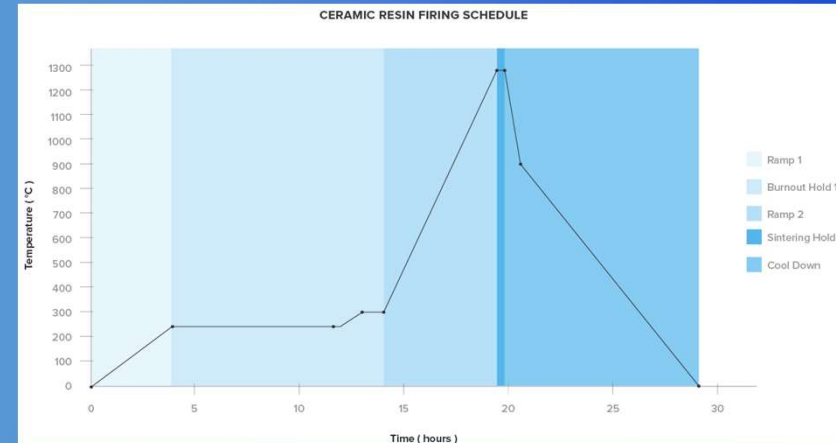
UTEP ExONE M-lab ZrC AM Trial 1

Heat Treatment

- Cure
 - Build envelope placed in oven.
 - 200 °C for 4 hrs in air then oven cooled to ambient temperature.
- Unpack and De-powder
 - “Green parts” removed from the powder bed
- Burn-out
 - Parts placed in high temperature graphite furnace
 - Ramp at 0.5 °C/min to 600 °C and hold for 1 hr.
 - Conducted in ultra-high purity argon and vacuum of 1×10^{-4} Torr.
- Sinter
 - Ramp at 30 °C/min to 1900 °C or 2000 °C and hold for 2 hrs.
 - Conducted in ultra-high purity argon and vacuum of 1×10^{-4} Torr.



NASA MSFC graphite furnace

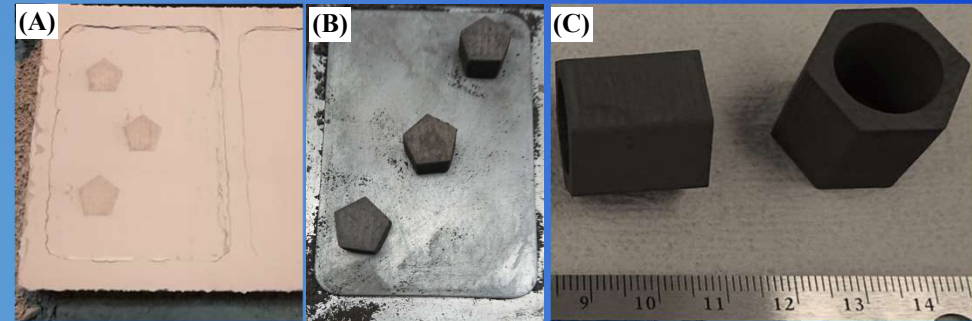


Example of a generalized ceramic heat treatment schedule. Courtesy Form Labs.

Specimen Characterization

- Geometric Variation

- Measured using digital calipers.
- CAD compared to as-built and HT.
- ΔXY (%) and ΔZ (%) changes determined for pre-print scale factors.



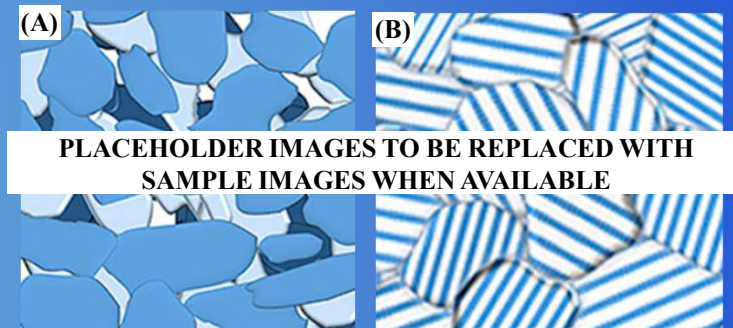
Specimens process (A), as-built AM ZrC specimens (B), and as-built tie-tube example AM parts (C).

- Density

- Measured using Archimedes' method or He pycnometry.
- Target: 60 %RD.

- Stoichiometry

- Target: slightly sub-stoichiometric ($C/Zr < 1$).
- If required additional heat treatment in the presence of H_2 could be used to modify stoichiometry.



Optical micrographs of ZrC specimens in the (A) as-built and (B) heat treated conditions.

Geometric variation vs. condition

Condition	Avg. Flat to Point (mm)	ΔXY (%)	Avg. Thickness (mm)	ΔZ (%)	Density (%RD)
CAD	11.18	-	7	-	-
As-built	11.3	+1.07	7.57	+8.14	41.506
HT1	10.955	-3.05	6.42	-15.19	54.0
HT2	10.870	-1.92	7.397	-1.20	TBD

Scalable AM Assessment

- Study to evaluate feasibility to increase production for larger scale utilization required for an NTP engine.
- Larger Binder Jet AM platform required
 - ExONE M-Flex: 400 x 250 x 250 mm.
 - Mlab to M-Flex requires moderate parameter translational adjustments.
 - Differences in powder deposition mechanism, layer timing, binder deposition rate, and build speed per layer (M-flex 35 vs. Mlab 60 sec).
 - Mlab envelope can fit 4 tie tube segments in one build.
 - M-Flex envelope can fit 1700 tie tube segments in one build.
- Large scale production viable
 - ~82 hrs for component production, not including final geometric shaping (grinding), non-destructive evaluation, geometric tolerance verification, etc.
 - Thousands of ZrC insulating segments required for NTP can be produced using a single existing production scale platform, oven, and furnace.



UTEP ExONE M-Flex Binder Jet AM machine

Conclusions

- Conclusions

- ZrC AM at desired density is feasible.
- Existing ZrC powder sufficient.
- Existing binder-jet AM platforms capable of meeting production needs.
- Availability of furnaces capable of reaching required temperature with required cleanliness is the primary constraint.
- Heat treatment schedules heavily influence part density, effective thermal conductivity, and compressive strength.
- Significant schedule delays resulted from Covid-19 social distancing protocols.

- Recommendations for future work

- Complete heat treatment optimization schedule to achieve desired density and sub-stoichiometry.
- Complete compression testing of heat treated specimens.
- Measure specimen effective thermal conductivity vs. density.
- Hot H₂ exposure testing of specimens and characterize resulting microstructure.
- Determine service life at operating conditions estimate.
- AM of full-size technology demonstrators and component level testing.

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