

Impact of Ceramic Nanoparticle Additions on the Properties of Additive Manufactured Refractory Metals *Carly Romnes*<sup>1</sup>, Toren Hobbs<sup>1</sup>, Fernando Reyes Tirado<sup>1</sup>, Jeffrey Sowards<sup>1</sup>, Omar Mireles<sup>2</sup>; James Stubbins<sup>3</sup>

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### Next-gen. nuclear energy systems require refractory metals



### Refractory alloy components are difficult and expensive to fabricate

These alloys have a variety of applications in extreme environments:

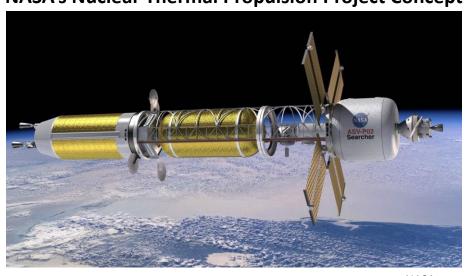
- Nuclear fusion systems (divertors, plasma facing components)
- ➤ Space nuclear power and propulsion
- ➤ Elevated temperature environments (>1500C)
- ➤ Aerospace systems and rocket nozzles
- > Hypersonic applications

Machining difficult

The HIDRA (Hybrid Illinois
Device for Research and
Applications) fusion device at
UIUC's Center for Plasma Facing
Materials Research

Fabrication expensive due to amount of waste





NASA.go



CPMI.Illinois.edu

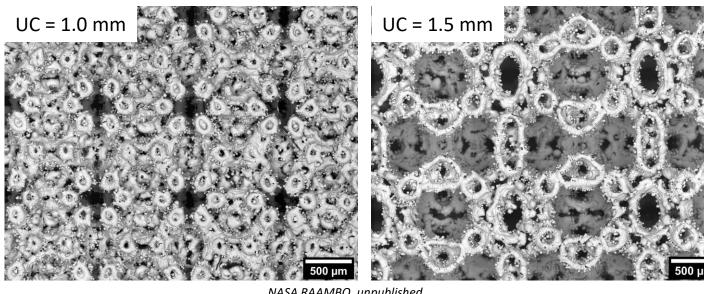
### AM of refractory metals has many benefits



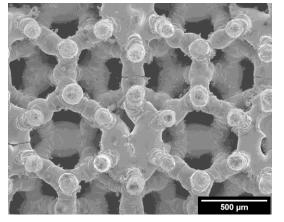
#### Additive manufacturing (AM) can help reduce fabrication expenses of refractory materials:

- Used to fabricate near-netshape components
- > Powder recycling reduces material waste and cost associated with fabrication
- > AM promotes fabrication of particularly complex structures

#### L-PBF molybdenum lattice structures with different unit cell (UC) sizes

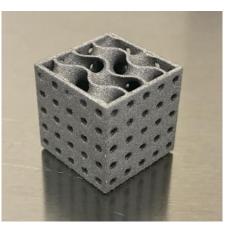


NASA RAAMBO, unpublished.



C. Romnes et al., JMEP 31(8) (2022), pg. 6256-6269.

L-PBF tungsten test print of nTop optimized heat exchanger design



Courtesy of B. Colon

2025 TMS Annual Meeting Background

L-PBF tungsten,

ultra-fine

lattice,

UC = 0.5 mm

### AM of pure refractory metals shows microcracking and porosity



#### After print parameter optimization, results still unfavorable

High thermal gradients and reheating result in residual stresses that can cause cracking

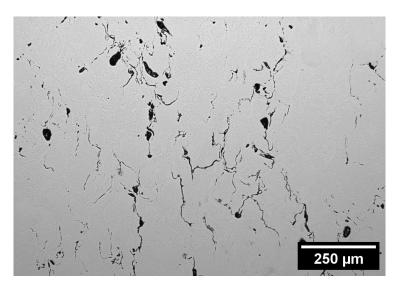
Brittleness of some metals results in stress-relief through microcracking

Porosity often due to lack of fusion

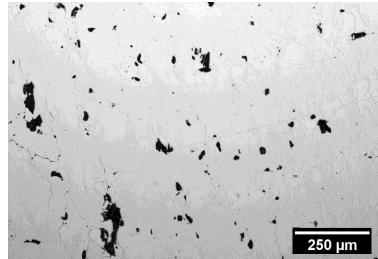
#### How to decrease cracking and porosity in AM refractory metals?

> Grain refinement

L-PBF **Tungsten** 



L-PBF Molybdenum



NASA RAAMBO, unpublished

**Build** Direction

### Current need for rigorous approach to AM refractory alloy design



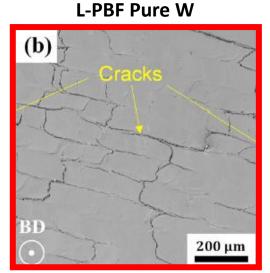
### Some work with adding ceramic dispersoids has shown promising results

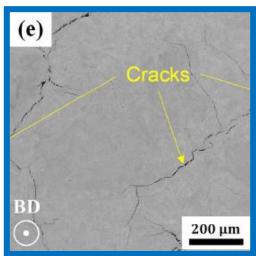
A few studies have shown that adding ZrC and TaC to tungsten AM feedstock helped reduce cracking

No justification for why the ceramic or the composition was chosen

L-PBF Pure W

L-PBF W + 5 wt% TaC





L-PBF Pure W L-PBFW + 0.5wt%ZrCa) BD BD 200 µm BD BD 100 µm 100 µm

J. Chen et al., JALCOM 897 (2022) 162978.

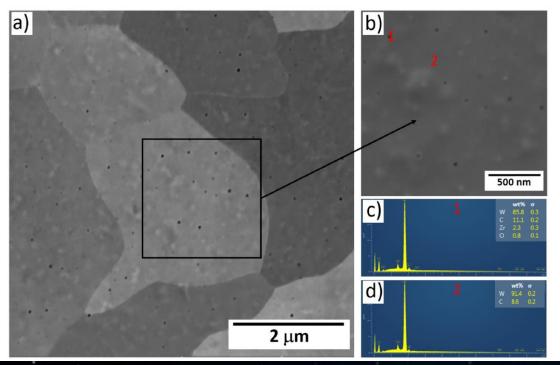
K. Li et al., IJRMHM 79 (2019), pg. 158-163.

### Direct impact of nanoparticle is unclear due to melting

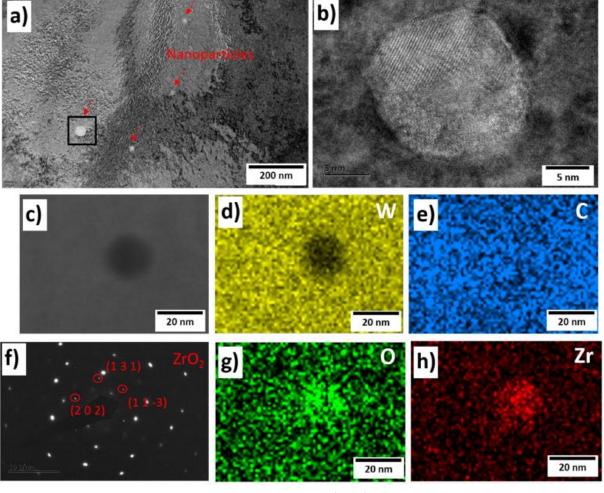


#### Nanoparticle melting can be caused by:

- ➤ Low nanoparticle melting temperature compared to base metal
- ➤ Melting temperature suppression of nanoparticles
- ➤ Aggressive print parameters
  L-PBF W + 0.5 wt% ZrC SEM-EDS results



L-PBF W + 0.5 wt% ZrC
STEM results showing ZrO<sub>2</sub> nanoparticle formation



### Direct impact of nanoparticle is unclear due to melting



### Nanoparticle melting can be caused by:

Low nanoparticle melting temperature compared to base metal

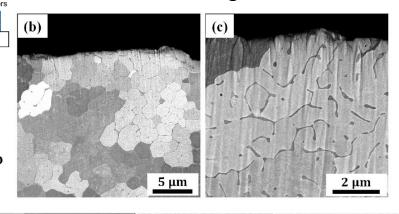
Substrate

Melting temperature suppression of nanoparticles

➤ Aggressive print parameters

Result is different compounds form, such well as cellular structures if large amounts added

L-PBF W + 5 wt% TaC SEM Images



(a)
(b) Righted cell'structures
(c) Nanobastoles

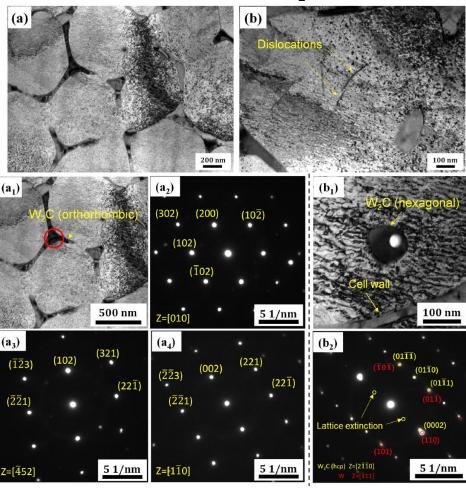
Nanobastoles

10 μm
(d)
(e)
(f)
Contribute side

Strike structures

J. Chen et al., JALCOM 897 (2022) 162978.

## L-PBF W + 5 wt% TaC TEM results showing hexagonal and orthorhombic W<sub>2</sub>C



### Current need for rigorous approach to AM refractory alloy design



The goal of this work is to prevent cracking and improve printability for AM of refractory metals

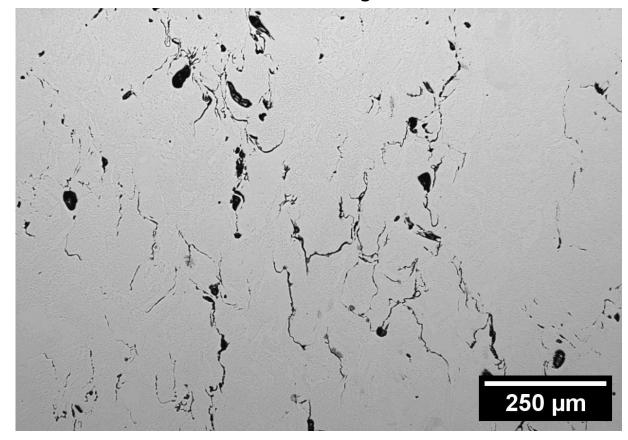
Identify and utilize computational tools to narrow down the experimental space

Utilize computational approaches for AM alloy design, validate with experimental work

Want to add small amount of other material, prevent large changes in properties

Is melting good or bad??

**L-PBF Pure Tungsten** 



NASA RAAMBO, unpublished.

### Nanoparticles can act as grain nucleation sites

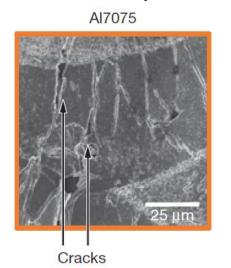


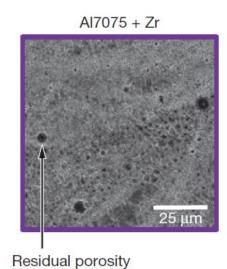
Schematic representing

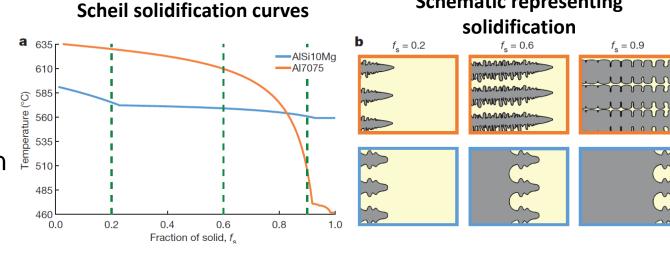
#### Nanoparticles added to AM feedstock can have multiple effects:

- ➤ Act as grain nucleation sites
- > Promotes equiaxed grains during fabrication

Al+Zr forms intermetallic compound early in solidification process

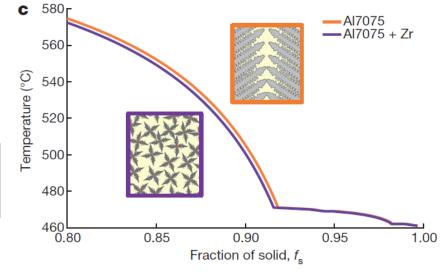






**Effect of adding ZrH** nanoparticles on cracking of AM AI7075

> Does not change **Scheil curves**



J. Martin et al., Nature 549 (2017), pg. 365-369.

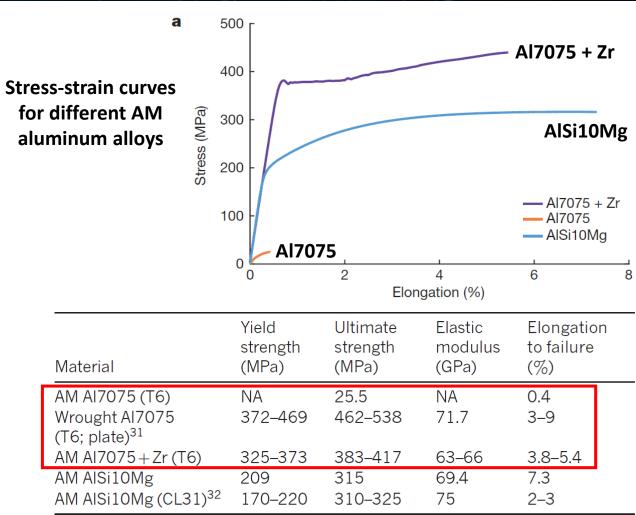
### Nanoparticles can act as grain nucleation sites



### Nanoparticles added to AM feedstock can have multiple effects:

- ➤ Act as grain nucleation sites
- > Promotes equiaxed grains during fabrication
- Reduces grain size, promoting decreased DBTT
- > Prevents grain growth by Zener pinning
  - Improves properties after HIP

These effects can result in increased strength, nearing the values of wrought metals



Measured and literature values for comparative alloys; ranges listed when available. 'T6' refers to the heat-treatment condition; 'plate' refers to the specific material; AM, additively manufactured; NA, not available.

J. Martin et al., Nature 549 (2017), pg. 365-369.

#### Is melting good or bad?



### Promising results but melting may result in smaller impact of nanoparticles

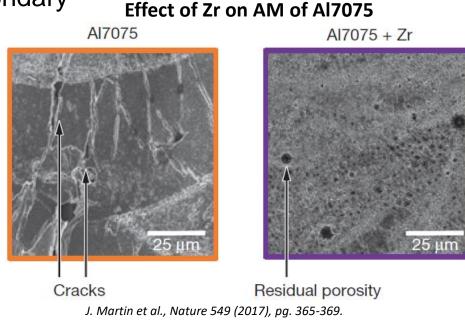
Bad because different phases formed

➤ New phases could be undesirable

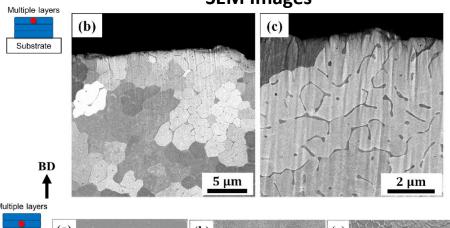
May be okay if secondary

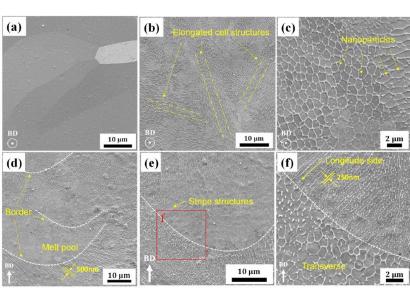
phase forms at beginning of solidification

How to best predict nanoparticle influence?



L-PBF W + 5 wt% TaC SEM Images





J. Chen et al., JALCOM 897 (2022) 162978.





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#### Material down-selection depends on application of interest



### Used nanoparticle melt temperature as initial selection criteria

➤ Should allow us to look at impact of solid nanoparticle vs. melted nanoparticle

Disqualified, $T_{m,ceramic} < T_{m,metal}$
Likely will melt, T <sub>m,ceramic</sub> < T <sub>m,metal</sub> + 100
Good candidate, $T_{m,ceramic} > T_{m,metal} + 100$

Base Metals	Tm (°C)				Pote	ntial (	CDS (T	m,CDS <sup>-</sup>	T <sub>m,me</sub>	etal)		
of Interest	1111 ( C)	WC	TiC	ZrC	NbC	TaC	HfC	SiC	VC	Mo2C	TaHfC	TaNbC
W	3410	-580	-250	10	198	470	490	-590	-610	-720	580	276
Mo	2610	220	550	810	998	1270	1290	210	190	80	1380	1076
Nb	2468	362	692	952	1140	1412	1432	352	332	222	1522	1218
Та	2996	-166	164	424	612	884	904	-176	-196	-306	994	690
Re	3180	-350	-20	240	428	700	720	-360	-380	-490	810	506
lr	2466	364	694	954	1142	1414	1434	354	334	224	1524	1220
C103 (Nb- based alloy)	2349	481	811	1071	1259	1531	1551	471	451	341	1641	1337

### Computational DOE determined by database availability



#### Not all material systems have been assessed for different databases available

➤ Material systems where database is critically assessed are best

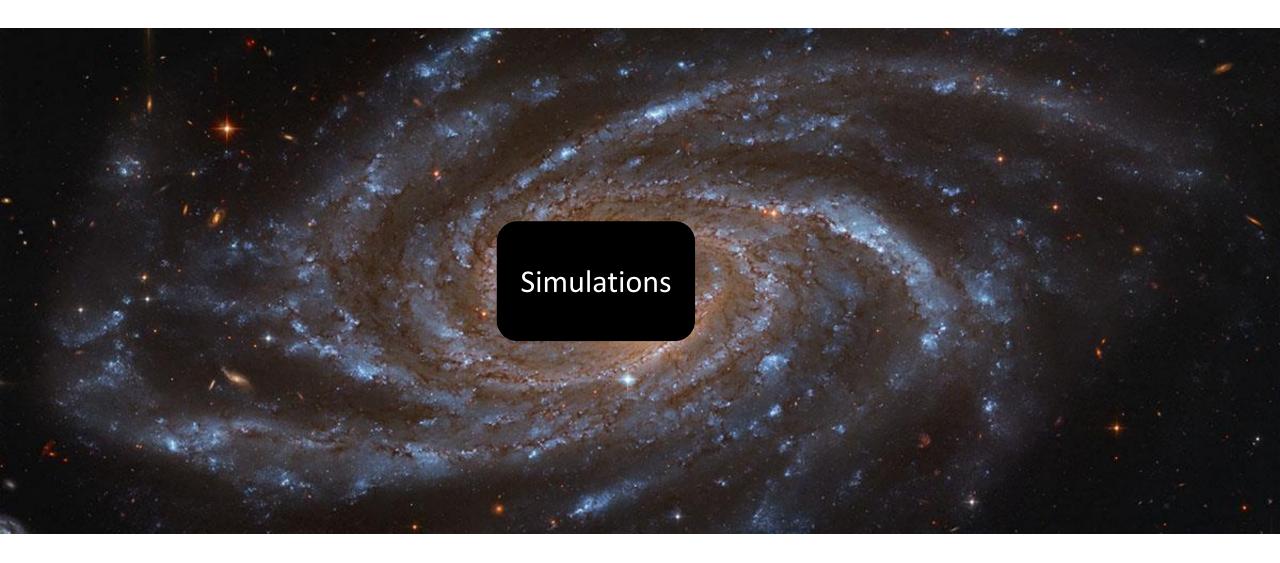
#### Additional selection criteria:

- > Cost
- ➤ Neutron absorption cross-section
- > Oxidation and corrosion resistance

Disqualified, no database available
May require verification
Well evaluated database available

Base Metals	Tm (°C)	Tm (°C) Potential CDS								
of Interest	1111 ( C)	WC	TiC	ZrC	NbC	TaC	HfC	SiC	VC	Mo2C
W	3410	HEA	HEA, Ni	Ni	HEA, Ni	HEA, Ni	Ni, HEA Tent		Ni	HEA, Ni
Mo	2610	HEA, Ni	HEA, Ni	HEA, Ni		HEA, Ni	HEA, Ni	Ni, HEA Tent	HEA, Ni	HEA
Nb	2468	HEA, Ni	HEA, Ni	Ni, HEA Tent	HEA	HEA Tent	HEA Tent		Ni, HEA Tent	
Та	2996	HEA	Ni	Ni	HEA Tent	HEA	Ni, HEA Tent			HEA, Ni
Re	3180	Ni, HEA Tent			HEA, Ni	Ni, HEA Tent	Ni		HEA Tent	HEA Tent
lr	2466									





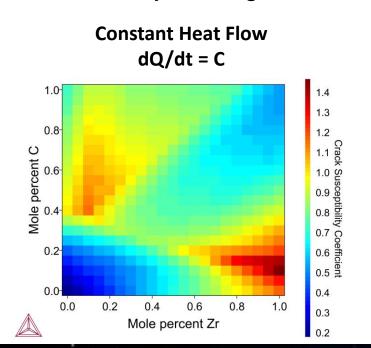
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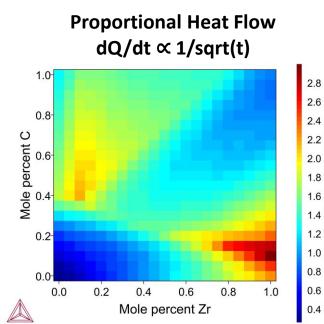
#### Several CSC approaches have composition at max values

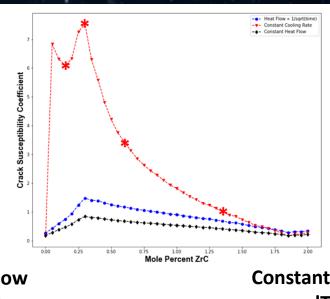


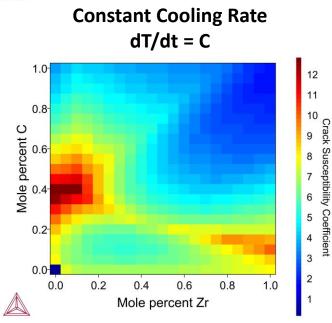
### Built in Crack Susceptibility Coefficient property modeler is used to predict hot cracking

- > Several options
- > Based on work of Yan and Lin
- > Recent update for Kou method
- > Essentially looking at worst case scenario









#### Similar trends seen for most materials



### CSC is highest at low amounts of the added material

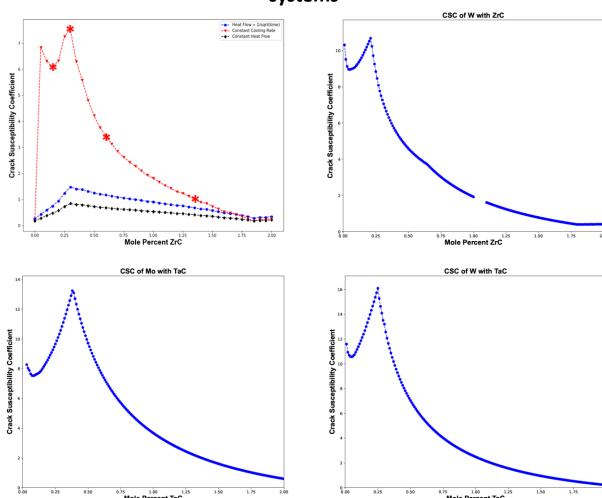
Developed DOE based on compositions obtained at same points along the curves:

- ➤ Composition less than that at max CSC
- ➤ Max CSC
- ➤ Max CSC/2
- ➤ Max CSC/4
- ➤ Max CSC = 1

Changed DOE some based on mixing results

**Used TCHEA6** 

### CSC Constant Cooling Rate curves for different material systems



### Large initial experimental DOE used



#### **Experimental DOE Based on CSC Results**

Material	CSI at Composition < Max	Max CSI	Max CSI/2	Max CSI/4	CSI ~ 1
Mo + ZrC	0.15 mol%	0.3 mol%	0.6 mol%	N/A	1.35 mol%
(400 – 1200 nm)	Heat-Treatment (HT)	HT	HT		HT
Mo + ZrC	0.15 mol%	0.3 mol%	0.6 mol%	N/A	1.35 mol%
(80 nm)	Print Param-Dev, HT	Print Param-Dev, HT	Print Param-Dev, HT		HT
Mo + ZrC	0.15 mol%	0.3 mol%	0.6 mol%	N/A	1.35 mol%
(20 nm)	Print Param-Dev, HT	Print Param-Dev, HT	Print Param-Dev, HT		HT
Mo + TaC (300 nm)	0.10 mol% Print Param-Dev, HT	0.38 mol% Print Param-Dev, HT	0.68 mol% Print Param-Dev, HT	N/A	N/A
W + ZrC	0.10 mol%	0.21 mol%	0.42 mol%	0.82 mol%	N/A
(400 – 1200 nm)	Print Param-Dev, HT	Print Param-Dev, HT	Print Param-Dev, HT	Print Param-Dev, HT	
W + TaC	0.10 mol%	0.24 mol%	0.46 mol%	0.76 mol%	N/A
(300 nm)	Print Param-Dev, HT	Print Param-Dev, HT	Print Param-Dev, HT	Print Param-Dev, HT	

#### Looked at Scheil curves for each composition

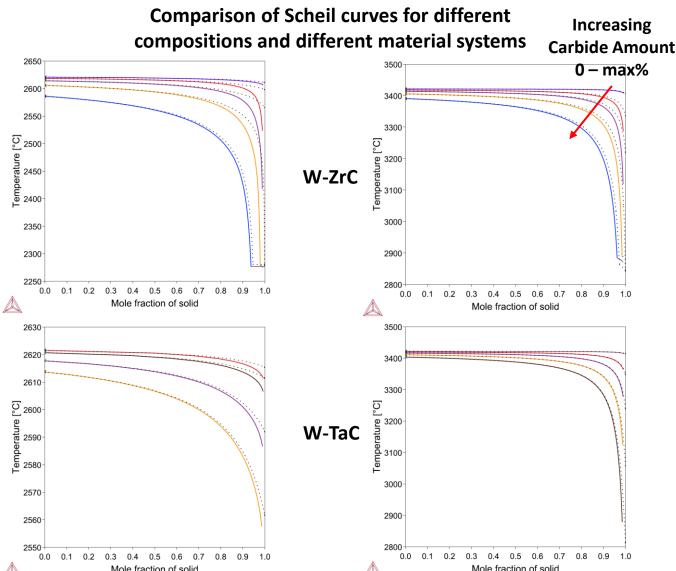


### Results show decreasing crack susceptibility as more material is added

If nanoparticle melts, predictions often showed a different phase solidifying

Mo-ZrC

- ➤ Databases do not have oxygen, needed for more accurate predictions
- ➤ New phases could be undesirable
- ➤ No way to predict if nanoparticle forms early on in solidification process using Scheil
- ➤ Can predict potential early-on formation by looking at the phase diagram
- Phase diagram helps with identifying carbide formation



#### Looked at phase diagrams to predict other phases formed

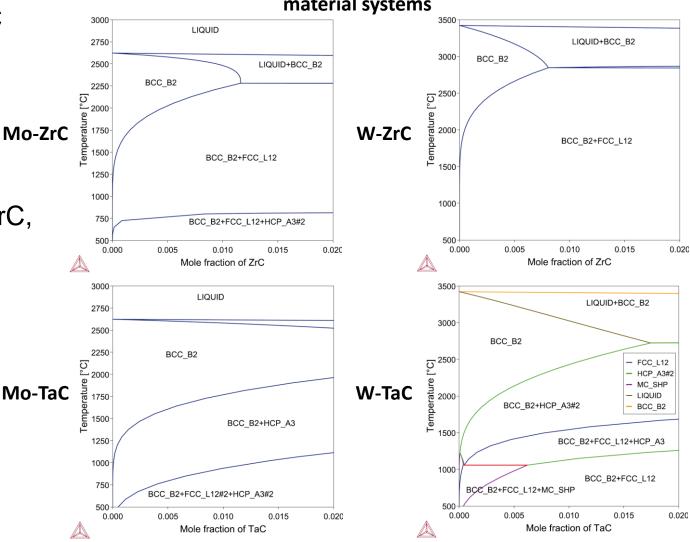


### Results with added ZrC tend to be more complicated than those with added TaC

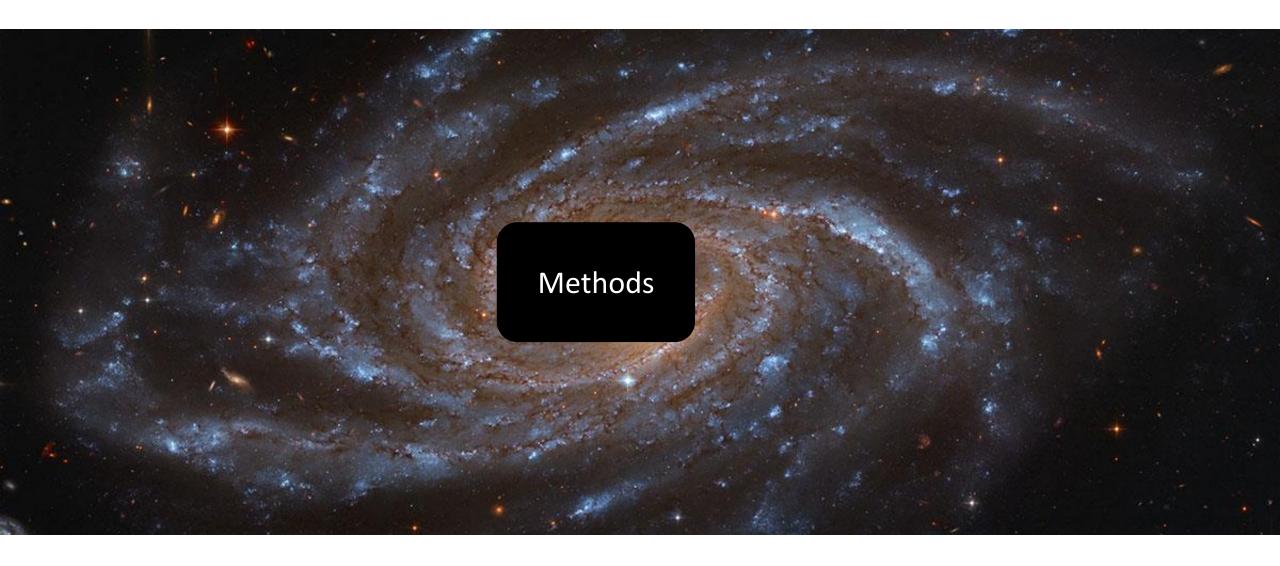
Looked at both binary and pseudo-binary phase diagrams

- ➤ Binaries: Mo-Zr, Mo-Ta, W-Zr, W-Ta
- Pseudo-binaries: Mo-ZrC, Mo-TaC, W-ZrC, W-TaC
- ➤ Mo-ZrC: ZrC forms first, then Mo<sub>2</sub>C
- ➤ Mo-TaC: Mo<sub>2</sub>C forms first, then TaC
- > W-ZrC: ZrC forms
- ➤ W-TaC: agrees with literature that W<sub>2</sub>C forms first

### Comparison of phase diagrams for different material systems







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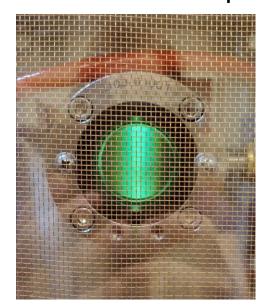
### Small L-PBF system used to reduce alloy development costs



### Plasma spheroidization may be required to prevent inhomogeneities due to sieving

Nanoparticles may detach during powder recycling

TEKNA TEKSPHERO-15 Plasma Spheroidizer





**EOS M100 Metal L-PBF System** 





### Acoustic mixing promotes uniform nanoparticle distribution



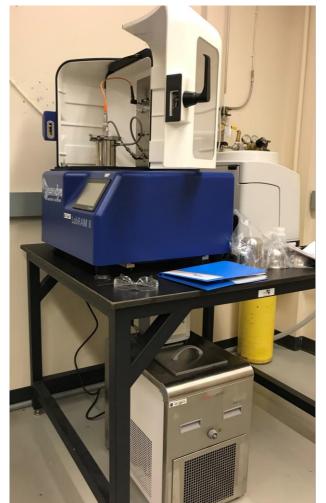
### Acoustic mixing is less aggressive than mechanical mixing methods

Homogenous mixture can be achieved for a variety of mixtures

Cooling fixture used to prevent powder overheating during mixing

Stainless steel vessel can also handle higher temperatures than plastic

Resodyn LabRAMII Acoustic Mixer with Cooling Fixture





#### Acoustic mixing prevents damage of spherical AM powder



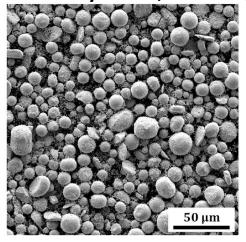
# Mechanical mixing techniques tend to cause difficulties with spheroidization

Acoustic mixing promotes uniform nanoparticle distribution

Spherical AM powder shows no damage after mixing

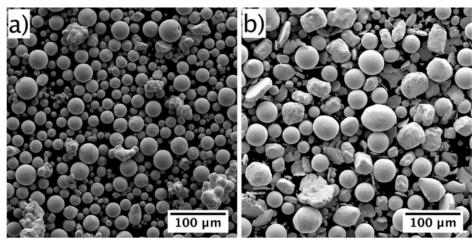
Particle size distribution does not change

Spherical W + 5wt% TaC (5 um)
Mechanically Mixed, low energy



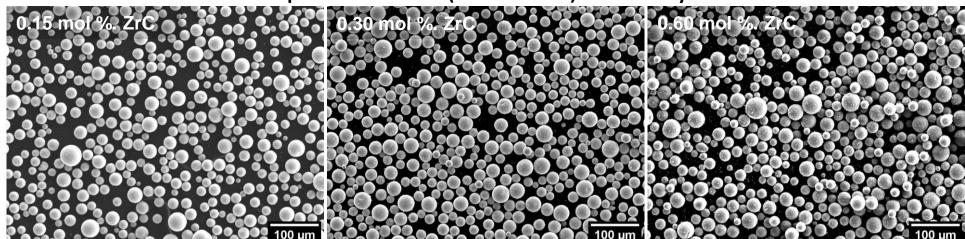
J. Chen et al., JALCOM 897 (2022) 162978.

a. W, and b. W + 0.5wt% ZrC Mechanically Mixed, then spheroidized



K. Li et al., IJRMHM 79 (2019), pg. 158-163.

#### Spherical Mo + ZrC (400-1200 nm) Acoustically Mixed



### Acoustic mixing does have limitations



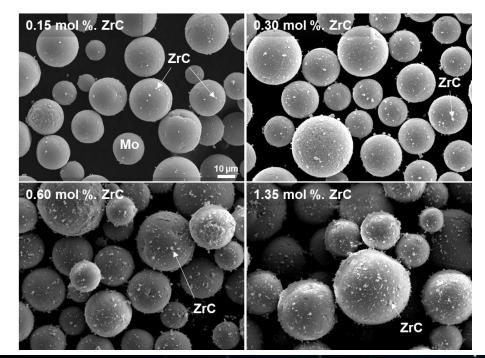
### Observed a saturation limit of nanopowder homogenously mixed

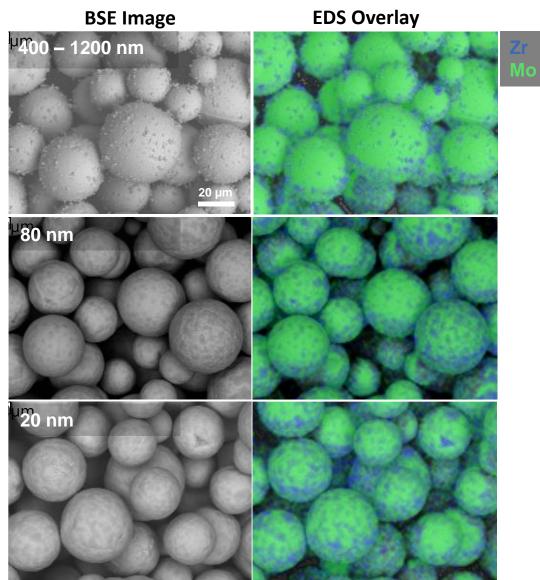
Caking of ZrC seen after mixing 0.6 mol% in Mo

➤ Saturation limit dependent on nanoparticle

size

Spherical Mo + ZrC (400-1200 nm) Acoustically Mixed





### TaC does not disperse similarly to ZrC



### TaC sticks to itself, resulting in TaC balls/agglomerates after mixing

Mo 0.10 mol% TaC

Mo 0.38 mol% TaC

Mo 0.38 mol% TaC

Mo 0.68 mol% TaC

Mo 0.68 mol% TaC

Mo 0.68 mol% TaC

#### Parameter optimization performed with slightly "complex" shape



### Specimen geometry allows us to evaluate print parameters for a more realistic shape

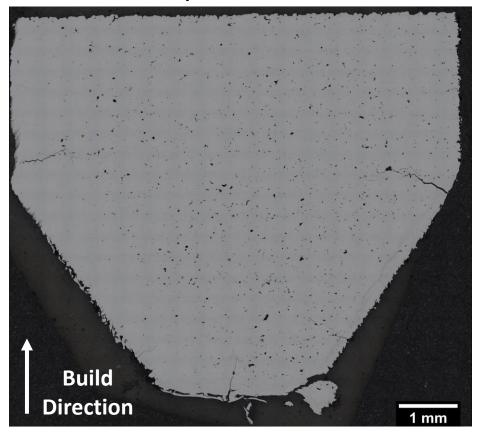
Build plate with several samples for parameter optimization



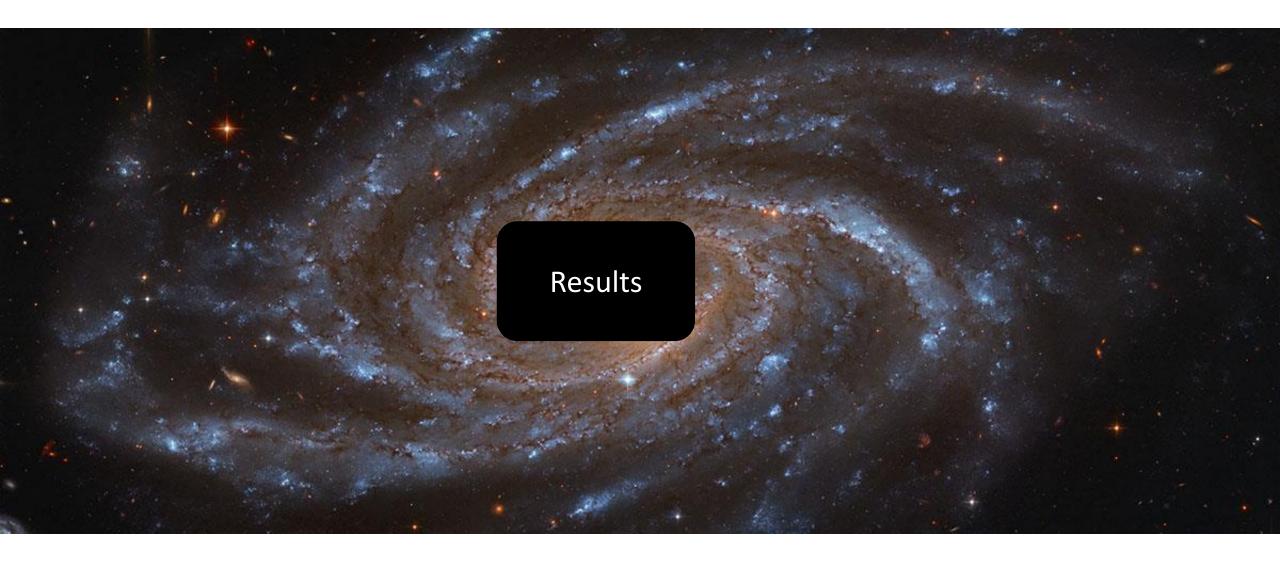
Example of parameter optimization sample burnout at build plate interface



**Example of parameter optimization** sample cross-section







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### Cracking much more prominent in tungsten

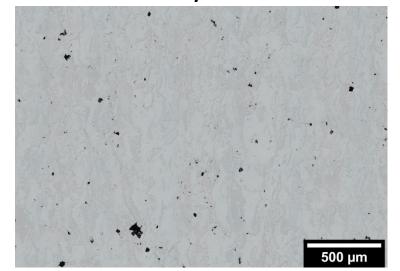


### Initial print parameter optimization performed on pure metal

He-pycnometer results higher than OM due to cracking

> He infiltrates the cracks

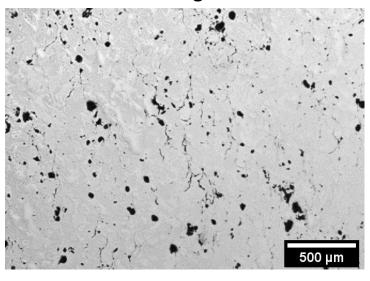
### Print parameters optimized for molybdenum



Density (He Pycnometer): 99.3 %TD
Density (Archimedes): 95.6 %TD
Density (OM Image Analysis): 99.2 %RD

Build Direction

Print parameters optimized for tungsten



Density (He Pycnometer): 99.5 %TD
Density (Archimedes): 96.7 %TD
Density (OM Image Analysis): 95.7 %RD

#### Experimental DOE summary



# Varied composition, print parameters, and performed HIP on one set of samples

A response to HIP is evidence of a reduction in cracking

HIP cannot be used on tungsten due to its high melting temperature

➤ HIP furnaces cannot reach temps required

Large DOE based on computational work

#### **Molybdenum Summary**

Dispersoid in Mo	Compositions	Print Parameters	Total Samples
ZrC 400-1200 nm	4	1	4
ZrC 80 nm	3	5	15
ZrC 20 nm	3	5	15
TaC 300 nm	3	5	15

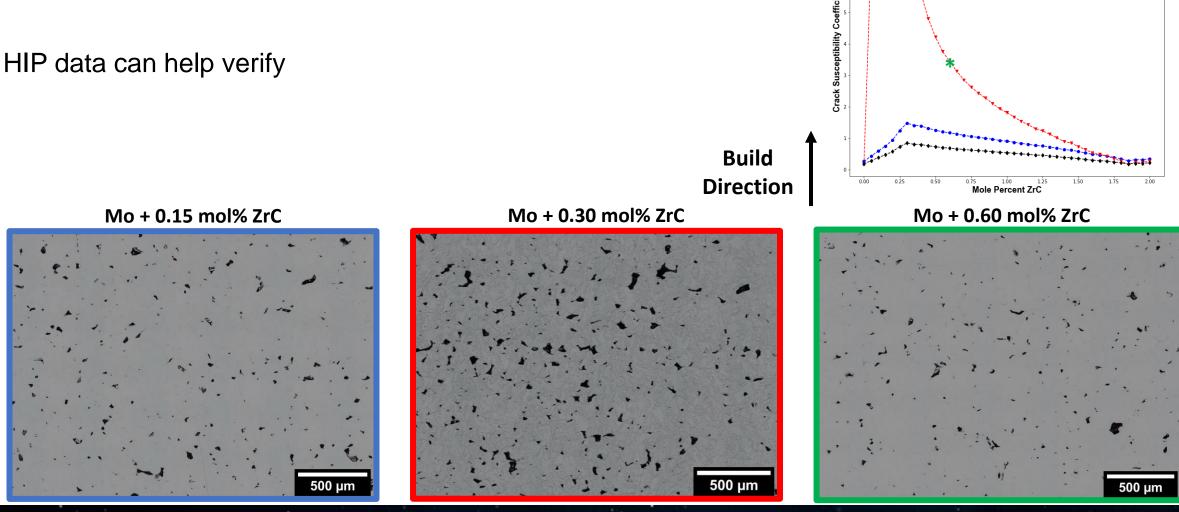
#### **Tungsten Summary**

Dispersoid in W	Compositions	<b>Print Parameters</b>	<b>Total Samples</b>
ZrC 400-1200 nm	4	5	20
TaC 300 nm	4	4	16

### Initial Mo-ZrC (400-1200 nm) results follow CSC trends



Thermo-Calc's CSC property modeler seems to reasonably predict results



**Experimental Results** 2025 TMS Annual Meeting

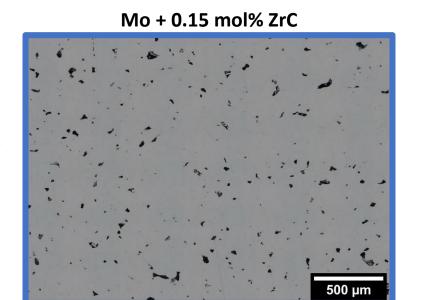
### Initial Mo-ZrC (400-1200 nm) results follow CSC trends

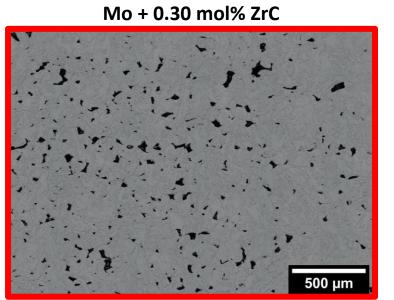


### Thermo-Calc's CSC property modeler seems to reasonably predict results

HIP data can help verify

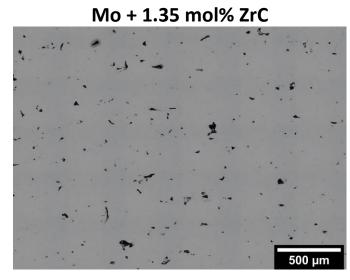
No large difference between 0.6 and 1.35 mol%

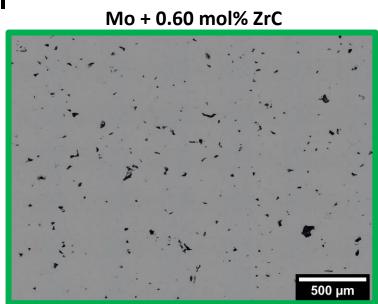




**Build** 

**Direction** 





### Initial Mo-ZrC (400-1200 nm) results show higher AB porosity

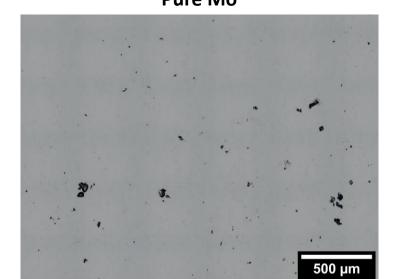


#### As-built density results using different methods all follow CSC trends

Mo + ZrC samples all had a higher porosity than pure Mo

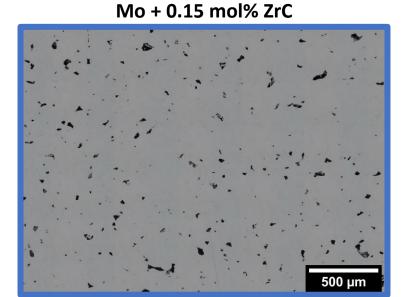
Mo-optimized parameters used

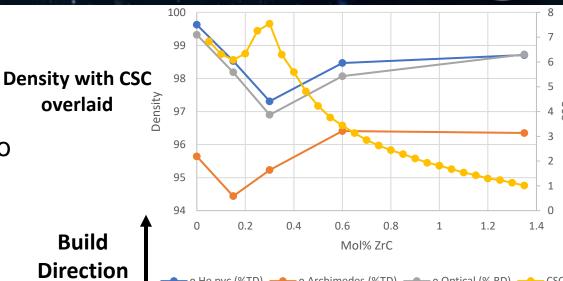
> Parameter optimization needed **Pure Mo** 

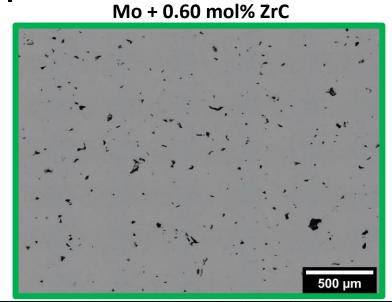


**Build Direction** 

overlaid







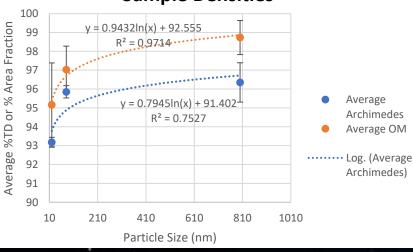
### Nanoparticle size has major effect on results

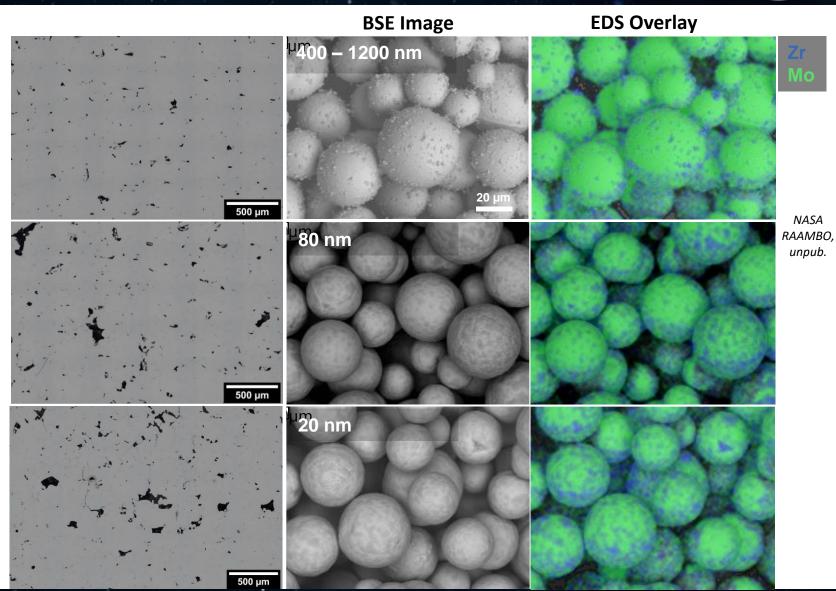


Decrease in density likely due to nanoparticle coverage affecting laser interaction during printing

Saturation limit also small effect

### Comparison of Mo-ZrC 1.35mol% Sample Densities





### Location of nanoparticles agglomeration changes based on size

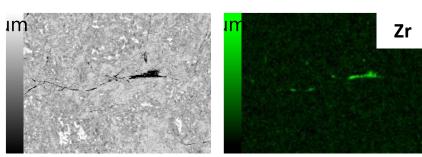


# Observed non-melted powder due to complete coating of <100 nm ZrC

Larger nanoparticle size seemed to agglomerate at the bottom of melt pools

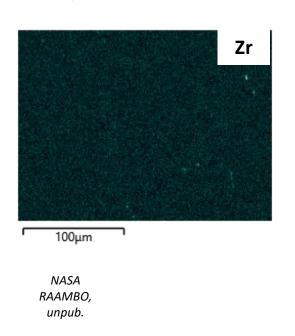
- ➤ Also seen in W-ZrC
- ZrC doesn't seem to melt in Mo but does agglomerate

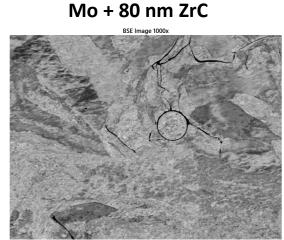
W-ZrC 0.82 mol% EDS

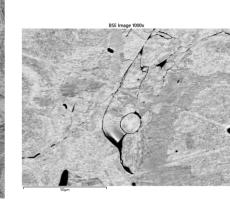


Mo + 400-1200 nm ZrC

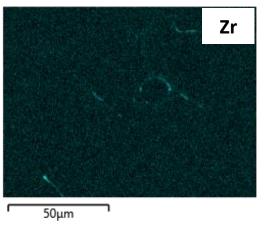
Electron Image 19

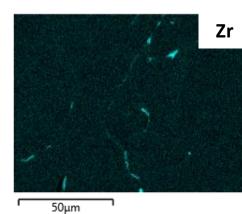






Mo + 20 nm ZrC

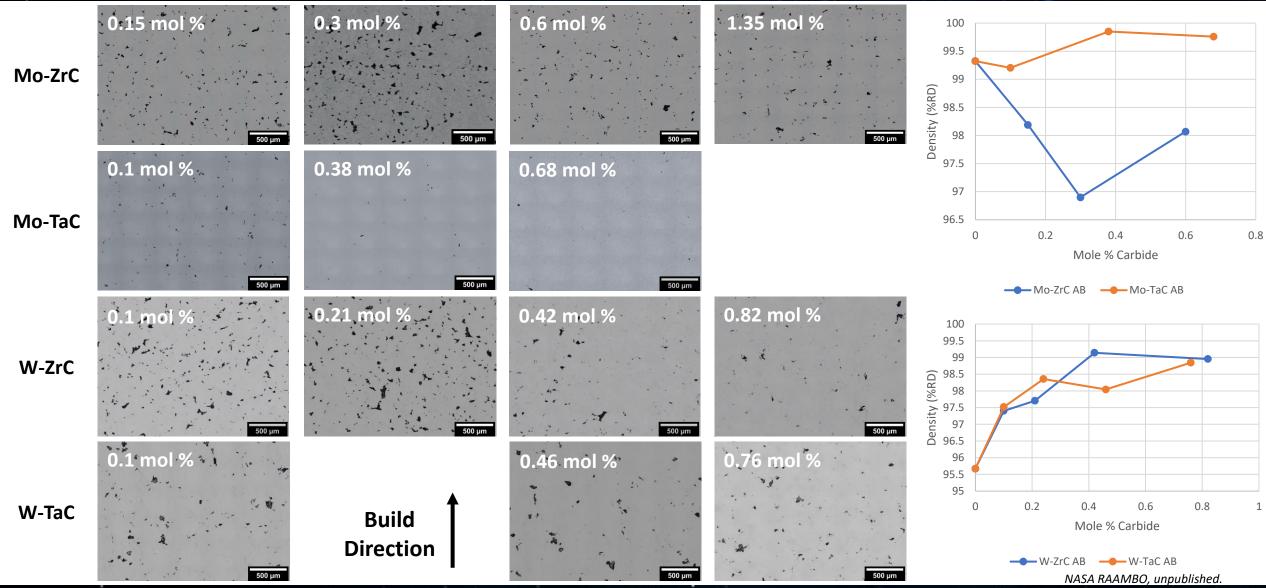




Build Direction

# As-built, experimental results summary for original print parameters



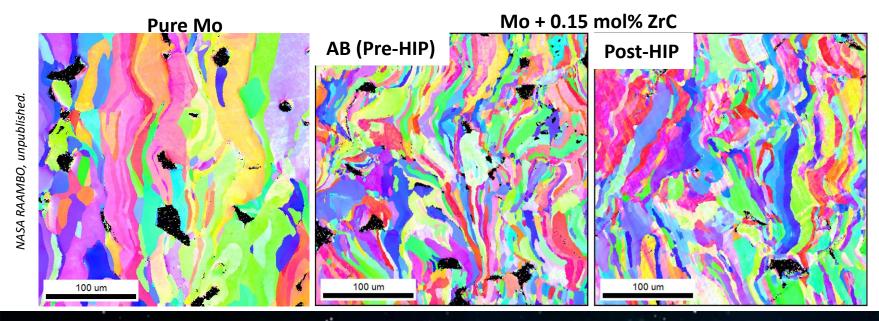


#### Initial Mo-ZrC (400-1200 nm) results show favorable HIP response

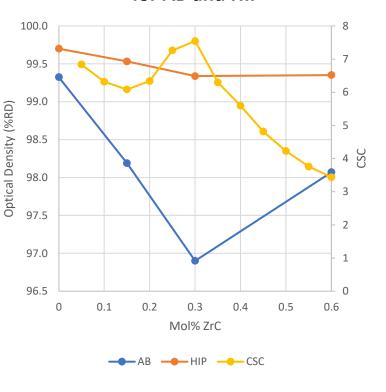


### EBSD shows smaller grain size in Mo-ZrC sample both in AB and HIP conditions

- ➤ Little to no grain growth observed after HIP heat treatment with ZrC added
- ➤ Large change in density seen, obtaining values close to pure Mo
- ➤ Work to be done on parameter-optimized samples



### Optical density measurements for AB and HIP





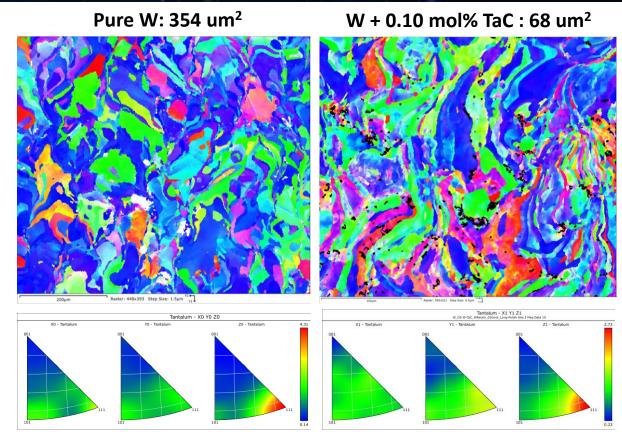
# VASA RAAMBO, unpublished.

# Initial Mo-TaC EBSD results show decreased grain size and less texturing



# EBSD shows smaller grain size in W-TaC sample with small addition of TaC (0.10 mol%)

- ➤ Cannot HIP tungsten so unable to determine grain growth due to high temp treatments
- Work to be done on parameter-optimized samples



Build Direction

#### Summary and Future Work

Thank you for your attention! Feel free to contact me with additional questions: carly.j.romnes@nasa.gov



Goal of this work is to reduce/prevent AM refractory alloy cracking through material design utilizing computational approaches

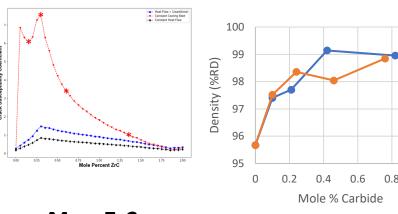
Experimental validation of computer simulations underway, issues identified

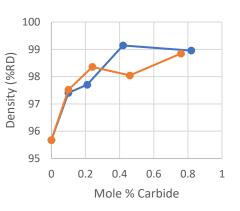
Pure metal print parameter optimization performed, in-process for carbide samples

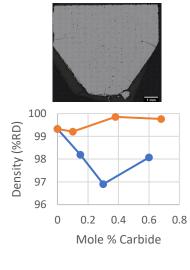
Initial results show promising trends, particularly after heat treatment

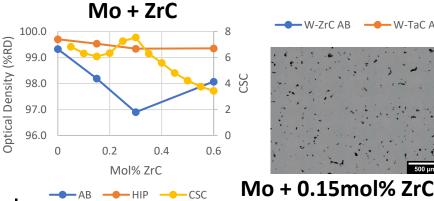
Investigate effects of dispersoids on mechanical properties

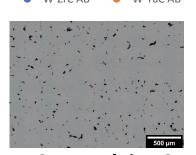
Further investigate effects of nanoparticle size and print parameters

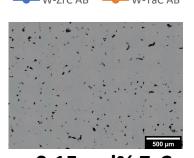




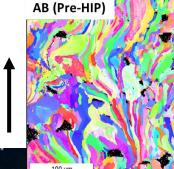








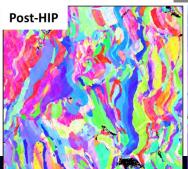
Pure Mo

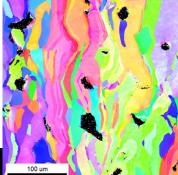


**Build** 

Direction

Summary





#### Summary and Future Work

# Thank you for your attention! Feel free to contact me with additional questions: carly.j.romnes@nasa.gov



Goal of this work is to reduce/prevent AM refractory alloy cracking through material design utilizing computational approaches

Experimental validation of computer simulations underway, issues identified

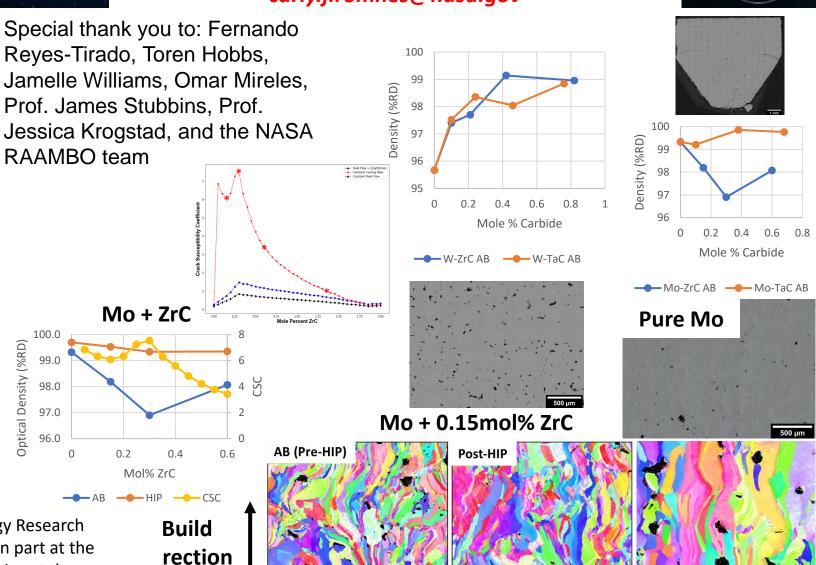
Pure metal print parameter optimization performed, in-process for carbide samples

Initial results show promising trends, particularly after heat treatment

Investigate effects of dispersoids on mechanical properties

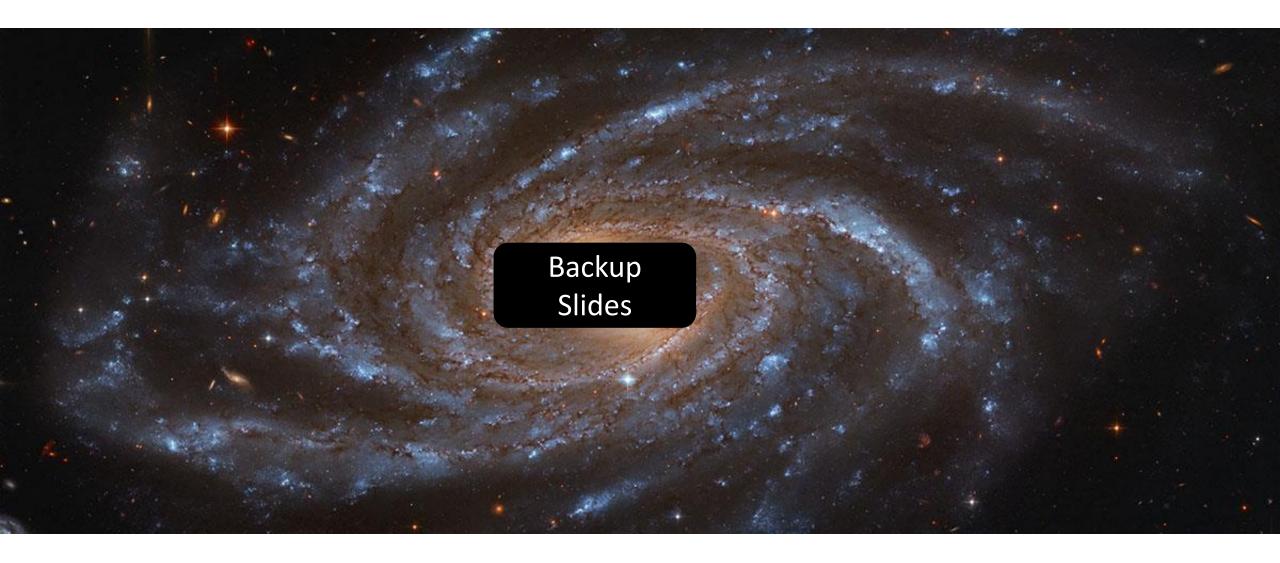
Further investigate effects of nanoparticle size and print parameters

This research is supported by a NASA Space Technology Research Fellowship, No. 80NSSC19K1168 and was carried out in part at the Materials Research Laboratory Central Research Facilities at the University of Illinois at Urbana-Champaign and the NASA Marshall Space Flight Center.



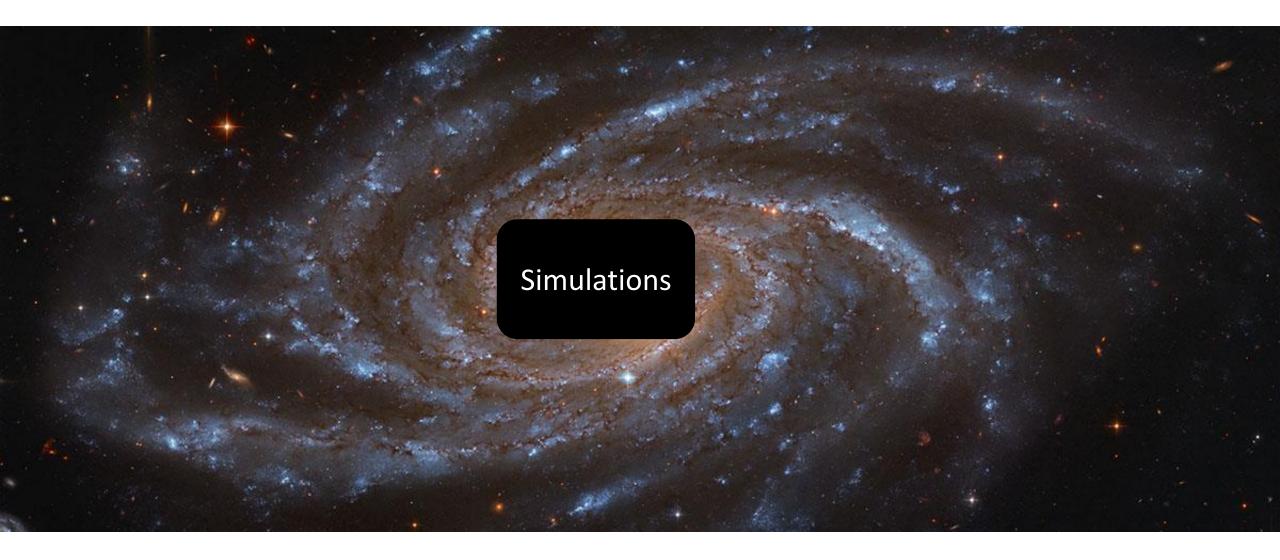
ımmary





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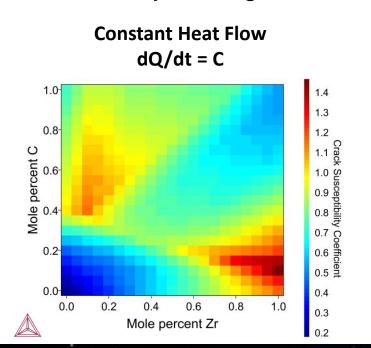
2025 TMS Annual Meeting 42

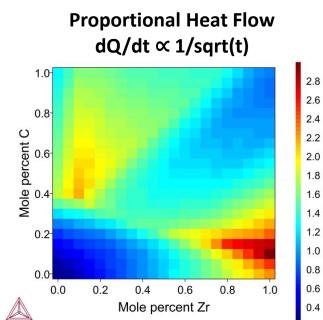
#### Several CSC approaches have composition at max values

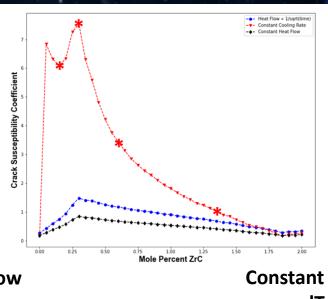


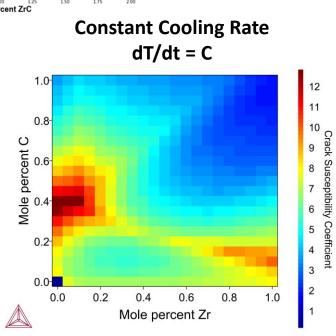
### **Built in Crack Susceptibility Coefficient property** modeler is used to predict hot cracking

- > Several options
- > Based on work of Yan and Lin
- > Recent update for Kou method
- > Essentially looking at worst case scenario







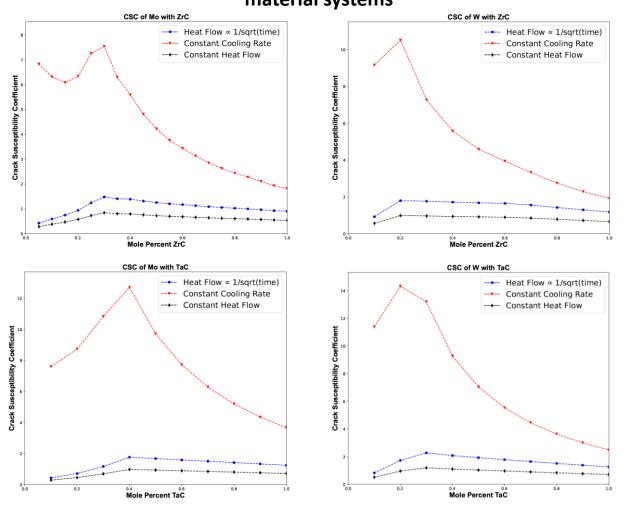


#### Similar trends seen for most materials



### CSC is highest at low amounts of the added material

### Comparison of CSC Values for different material systems



### Large initial experimental DOE used



#### **Experimental DOE Based on CSC Results**

Material	CSI at Composition < Max	Max CSI	Max CSI/2	Max CSI/4	CSI ~ 1
Mo + ZrC	0.15 mol%	0.3 mol%	0.6 mol%	N/A	1.35 mol%
(400 – 1200 nm)	Heat-Treatment (HT)	HT	HT		HT
Mo + ZrC	0.15 mol%	0.3 mol%	0.6 mol%	N/A	1.35 mol%
(80 nm)	Print Param-Dev, HT	Print Param-Dev, HT	Print Param-Dev, HT		HT
Mo + ZrC	0.15 mol%	0.3 mol%	0.6 mol%	N/A	1.35 mol%
(20 nm)	Print Param-Dev, HT	Print Param-Dev, HT	Print Param-Dev, HT		HT
Mo + TaC (300 nm)	0.10 mol% Print Param-Dev, HT	0.38 mol% Print Param-Dev, HT	0.68 mol% Print Param-Dev, HT	N/A	N/A
W + ZrC	0.10 mol%	0.21 mol%	0.42 mol%	0.82 mol%	N/A
(400 – 1200 nm)	Print Param-Dev, HT	Print Param-Dev, HT	Print Param-Dev, HT	Print Param-Dev, HT	
W + TaC	0.10 mol%	0.24 mol%	0.46 mol%	0.76 mol%	N/A
(300 nm)	Print Param-Dev, HT	Print Param-Dev, HT	Print Param-Dev, HT	Print Param-Dev, HT	

#### Looked at Scheil curves for each composition

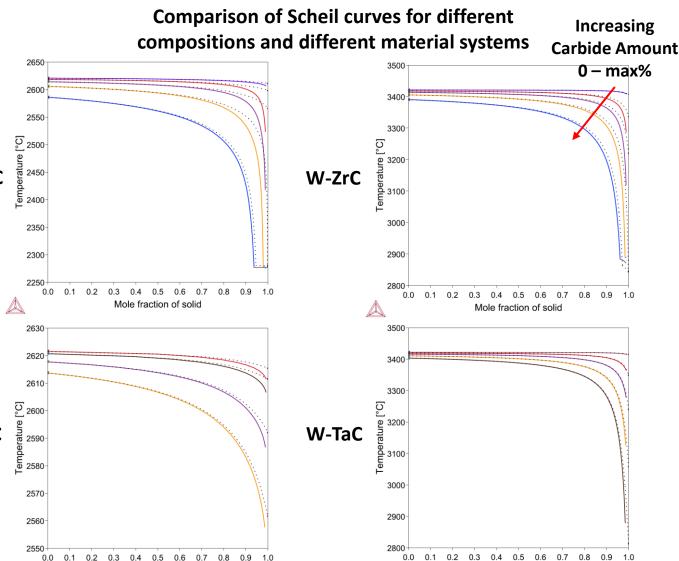


### Results show decreasing crack susceptibility as more material is added

If nanoparticle melts, predictions often showed a different phase solidifying

Mo-ZrC

- ➤ Databases do not have oxygen, needed for more accurate predictions
- ➤ New phases could be undesirable
- ➤ No way to predict if nanoparticle forms early on in solidification process using Scheil
- ➤ Can predict potential early-on formation by looking at the phase diagram
- Phase diagram helps with identifying carbide formation



Computational Results

#### Looked at phase diagrams to predict other phases formed



### Results with added ZrC tend to be more complicated than those with added TaC

Looked at both binary and pseudo-binary phase diagrams

- ➤ Binaries: Mo-Zr, Mo-Ta, W-Zr, W-Ta
- Pseudo-binaries: Mo-ZrC, Mo-TaC, W-ZrC, W-TaC
- ➤ Mo-ZrC: ZrC forms first, then Mo<sub>2</sub>C
- ➤ Mo-TaC: Mo<sub>2</sub>C forms first, then TaC
- > W-ZrC: ZrC forms
- ➤ W-TaC: agrees with literature that W<sub>2</sub>C forms first

### Comparison of phase diagrams for different material systems

