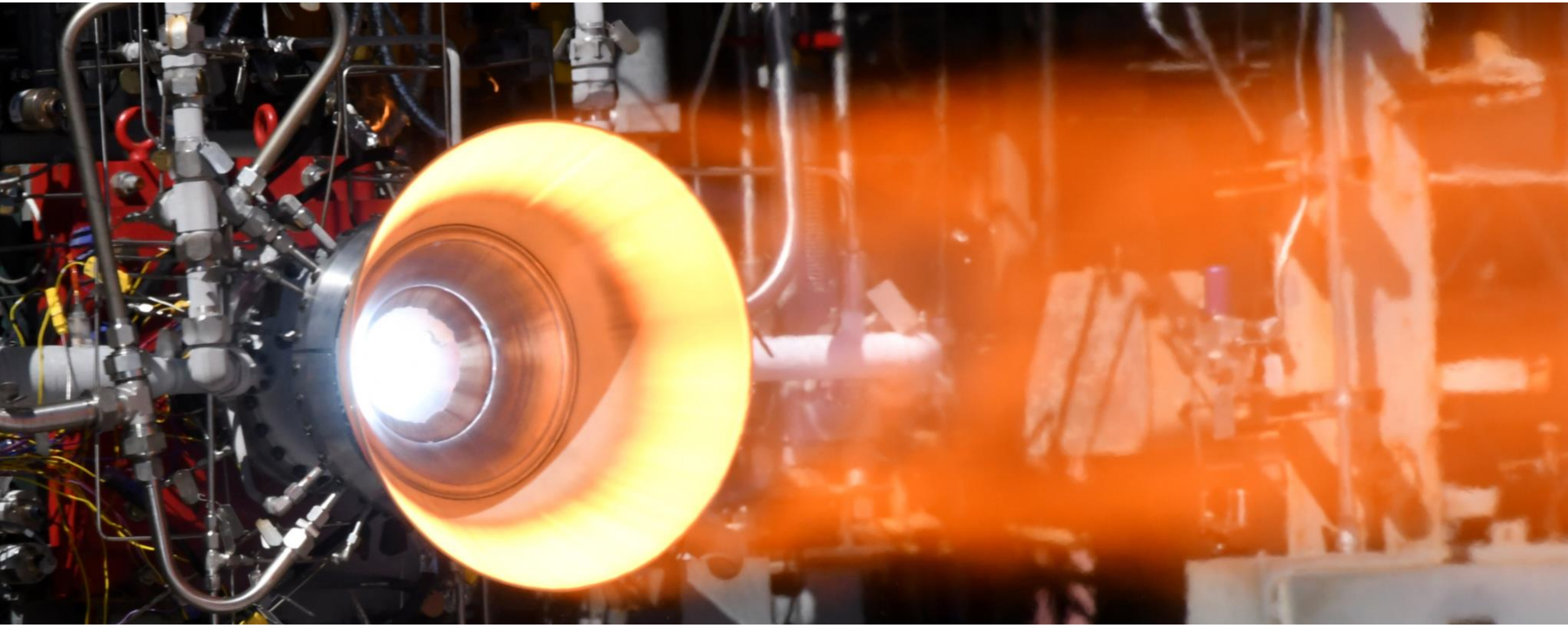
Evaluation of In-Situ Alloyed, Additively Manufactured GRCop-42



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Additionally, this work would not be possible without our excellent colleagues at:

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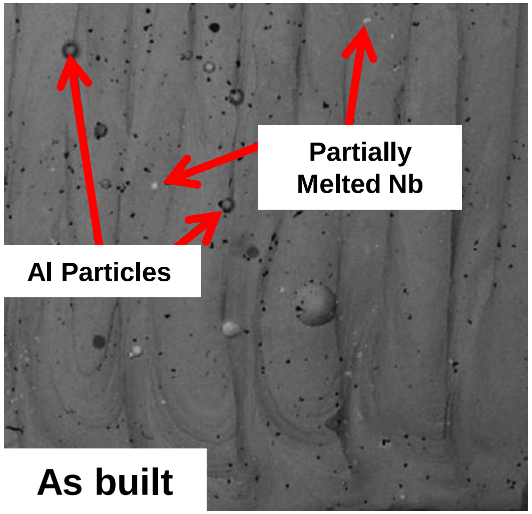
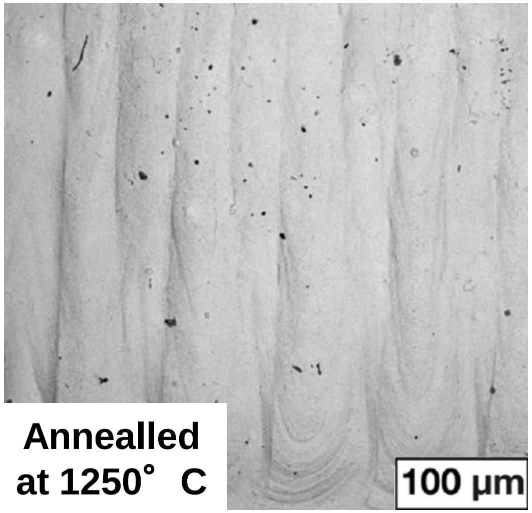
Overview

- Background
- Powder Manufacturing
- Parameter Mapping
  - Fractography for Parameter Optimization
  - Porosity Results
- Phase Extractions
  - Procedure
  - Laser Parameter Results
  - Phase/Chemical Results
  - Morphology Results
- Conclusions

Background: AM In-Situ Alloying

- Current Literature:
  - Binary or ternary intermetallic alloys.
    - All elements participate in the reaction (Ti-Al, Ti-Al-Nb, Ti-B, etc.)
  - Post-processing can be used to “fix” microstructural issues, shown right.
- Our work:
  - Dispersion-strengthened alloy
    - Cu does not participate in the alloying process
    - Reacting Cr_2Nb in melt pool
  - Heat treatment cannot necessarily be used to “fix” microstructure
    - Nb has little diffusivity in solid Cu

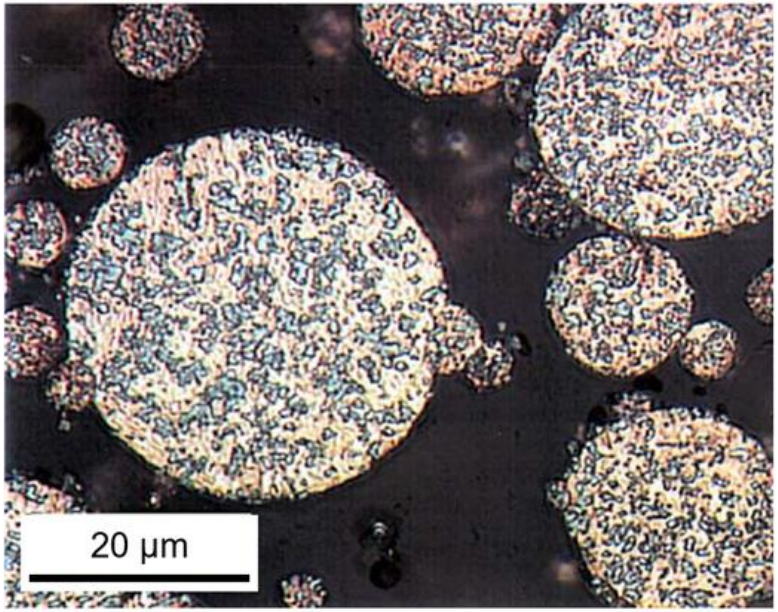




[1]A. Grigoriev, et al. J. Alloys Compd, 2017 Vol 704, p 434-442.

Background: GRCop

- Family of Cu-Cr-Nb alloys with pure Cu matrix with Cr_2Nb dispersoid
    - GRCop-42: Cu-4 at% Cr-2 at% Nb
    - Conventionally processed by gas atomization.
- Designed for:
    - High temperature mechanical properties
    - High thermal conductivity[1]
- Additive manufacturing (AM) provides increased design freedom and advanced alloying capabilities
- Challenges:
    - Nb diffusivity in solid Cu is very low.
    - High reflectivity of Cu makes most lasers a challenge to work with.
        - Green laser or e-beam is preferred, but not always available.



[3]D. L. Ellis, NASA TM - 2005-213566, 2005.

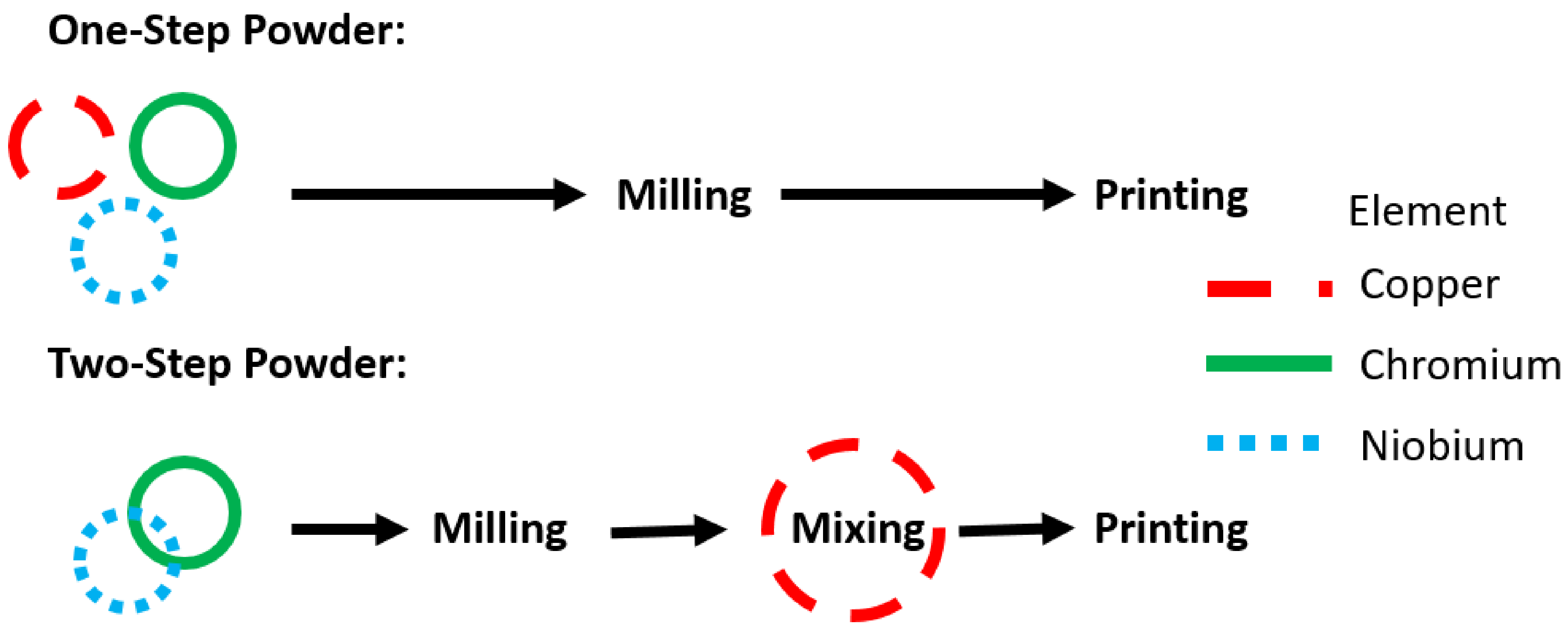
[2] K. G. Cooper, et al. NASA TM -2018-220129, 2018.

Goals

- Facilitate GRCop component manufacturing by eliminating the gas atomization process in GRCop alloying
  - React Cr and Nb to form Cr_2Nb in Cu matrix in situ during AM
  - No excess elemental Nb
    - Nb highly susceptible to H embrittlement
  - Achieve similar mechanical characteristics to additively manufactured GRCop alloyed via gas atomization

- Identify key characteristics that influence in situ alloying
  - Can these be applied to other alloys?

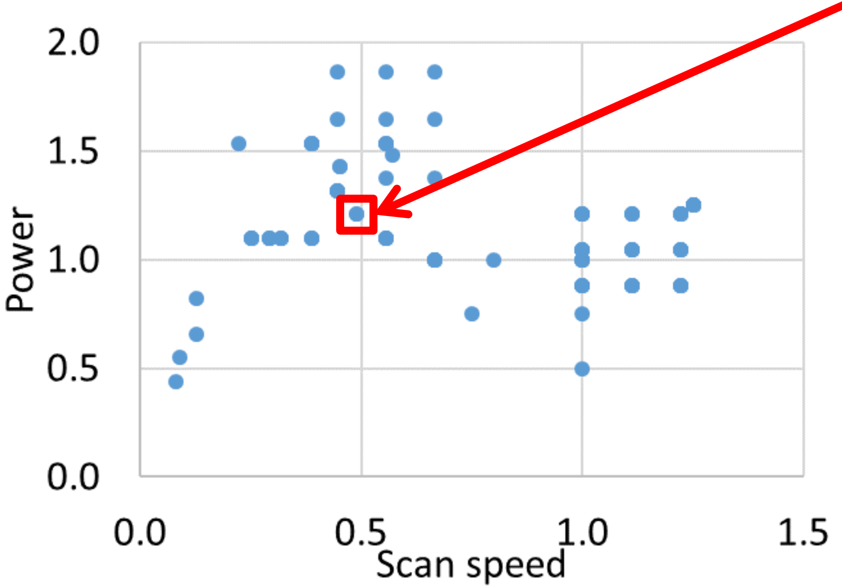
Elemental Powder Preparation

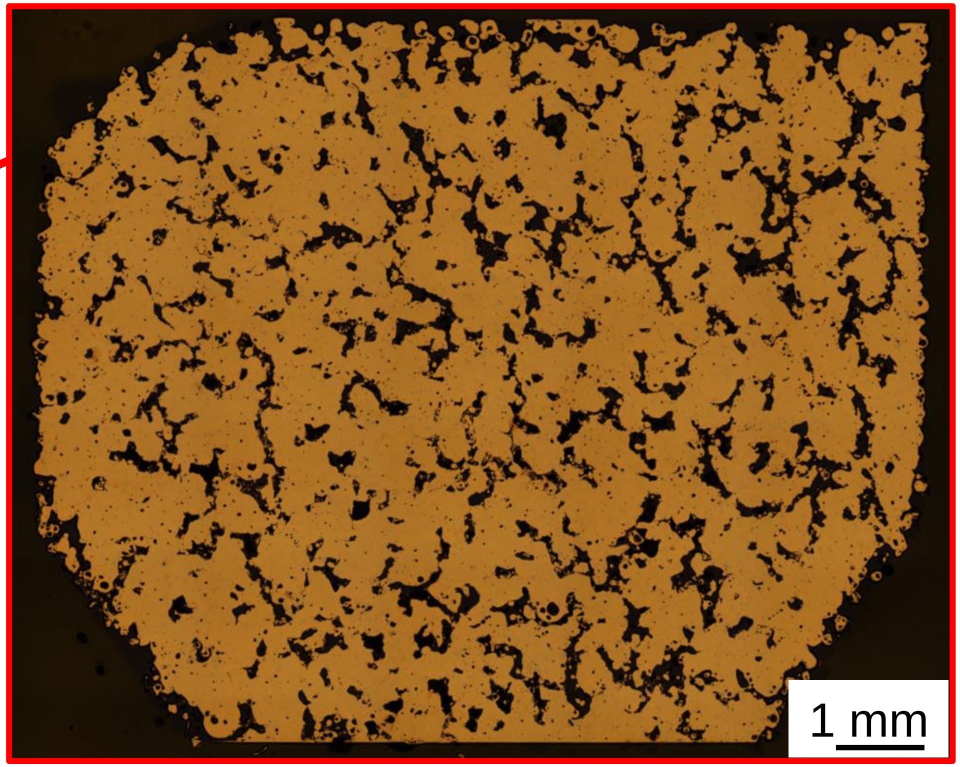


- Two-step powder processing creates more contact between Cr and Nb, which should facilitate the formation of Cr_2Nb

Parameter Mapping

- High porosity detected in the printed materials.
- Cu has high reflectivity in 1064 nm wavelength used by EOS M100.
- Best density was 95%, which is too high to HIP out and retain dimensional fidelity.

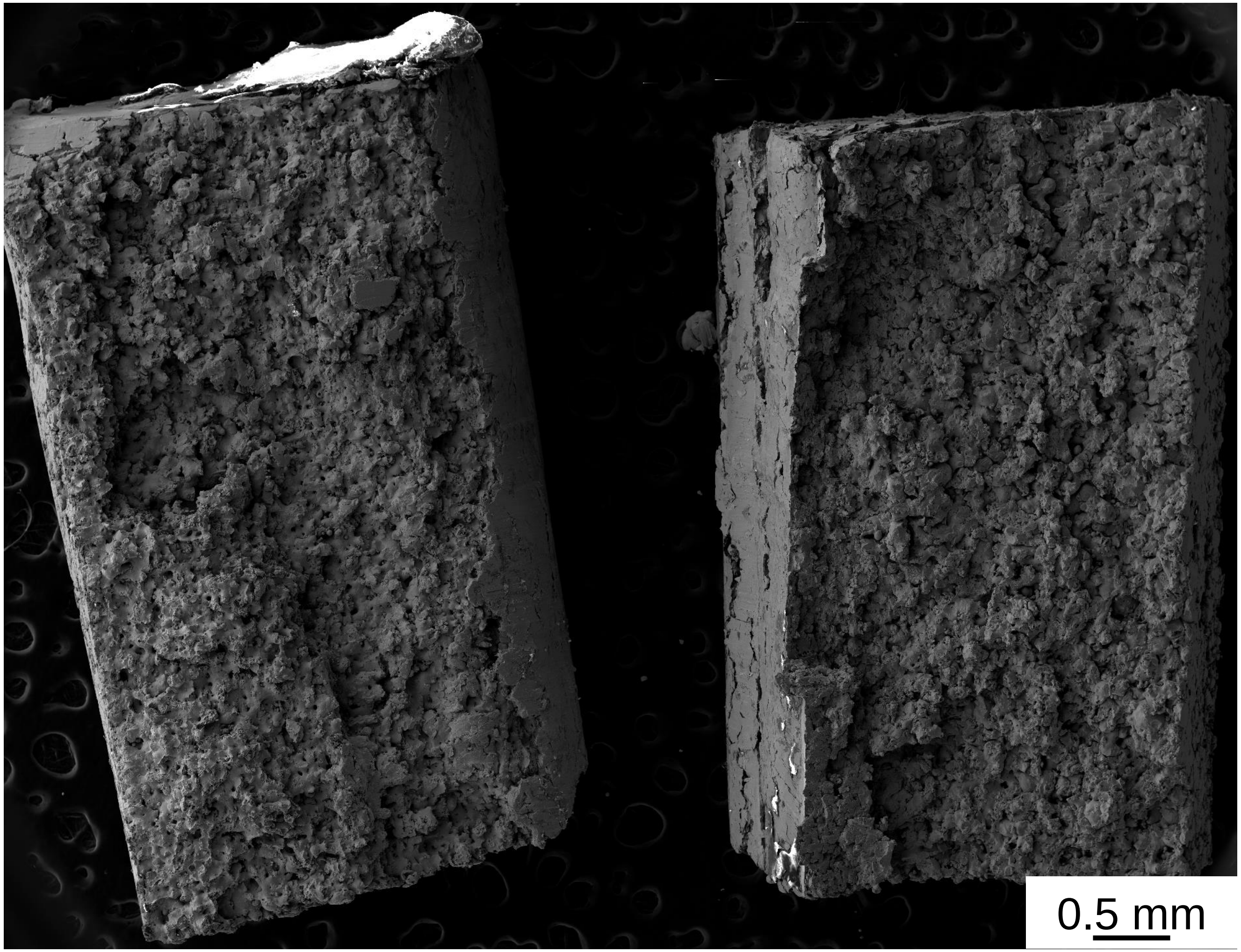




Fractography to Image Porosity Details

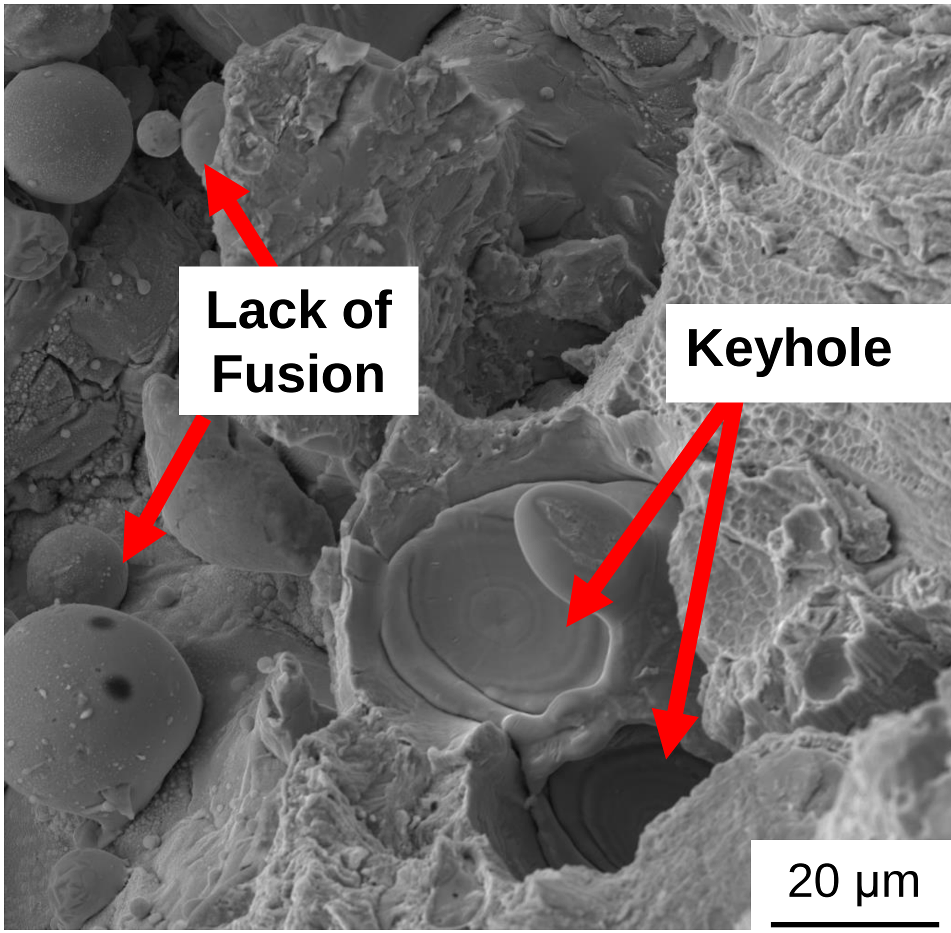
- Fatigue provides fracture surfaces with unique lack of fusion and keyhole defects.

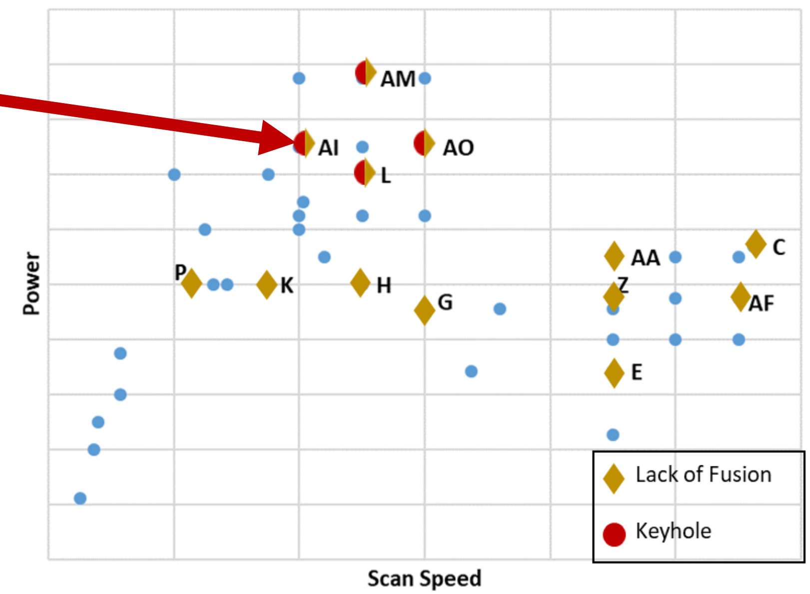
- These defects can provide insight on what needs to change to optimize the parameters.



Scannapieco, et al. “Fracture Surface Defect Quantification for LPBF Additively Manufactured Ti-6Al-4V” MS&T2021. Monday 10/18/2021.

Fractography to Image Porosity Details





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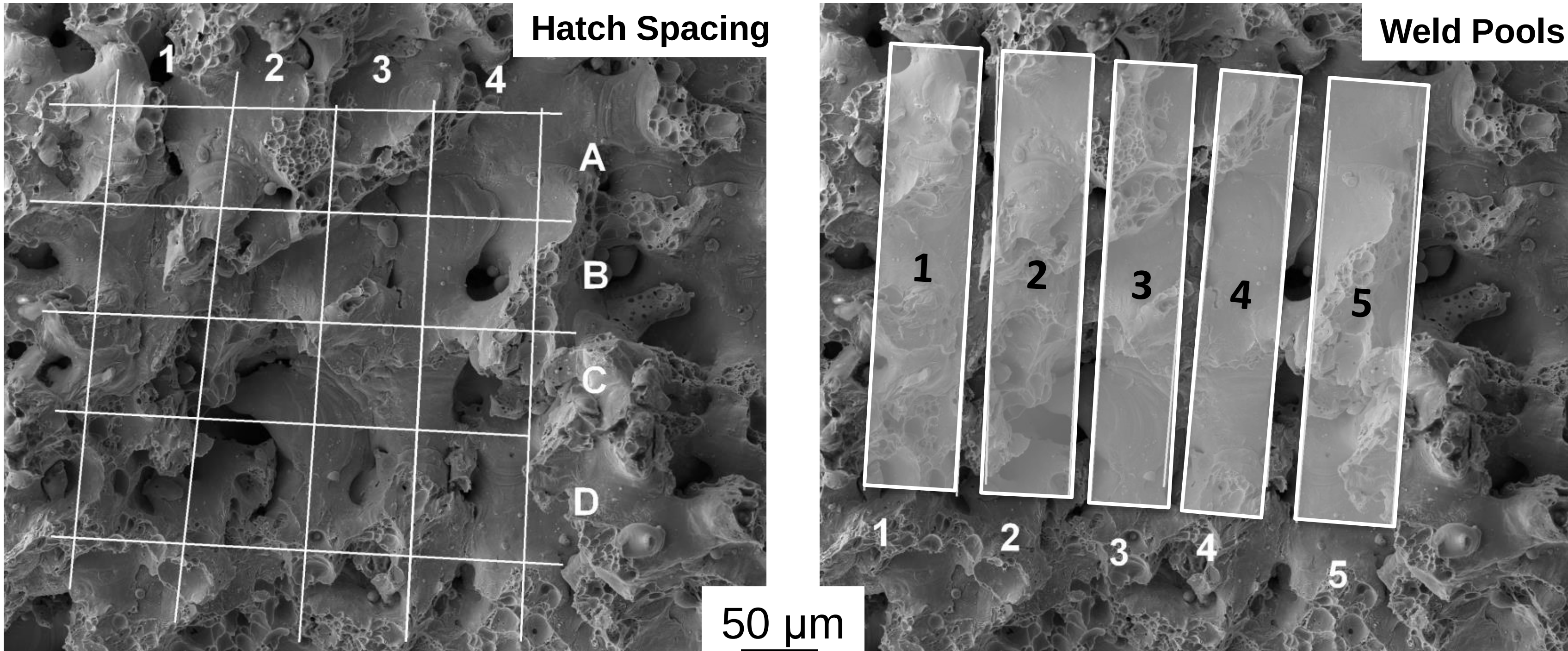
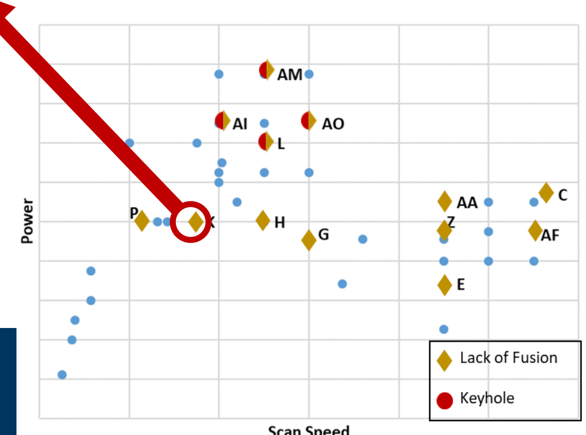
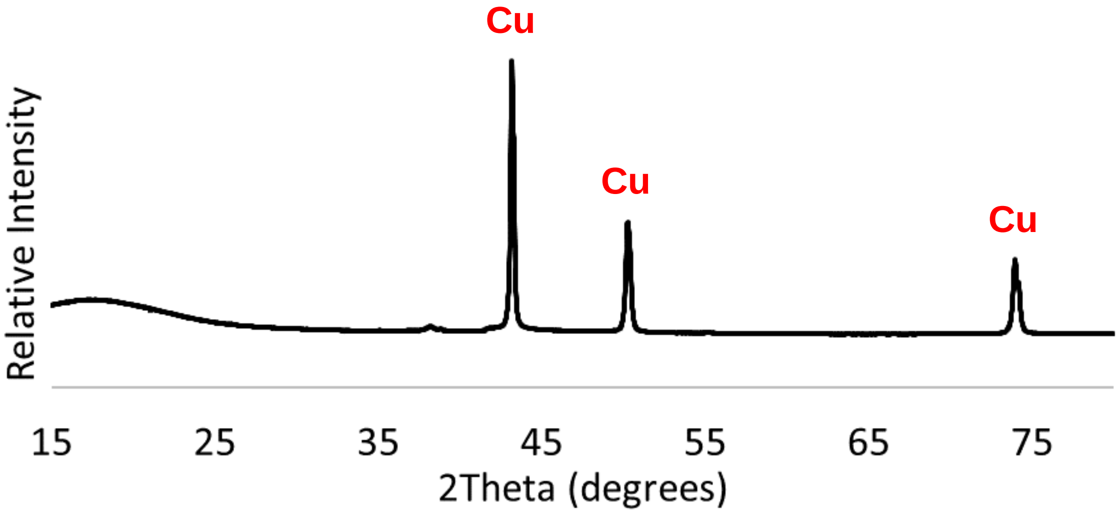


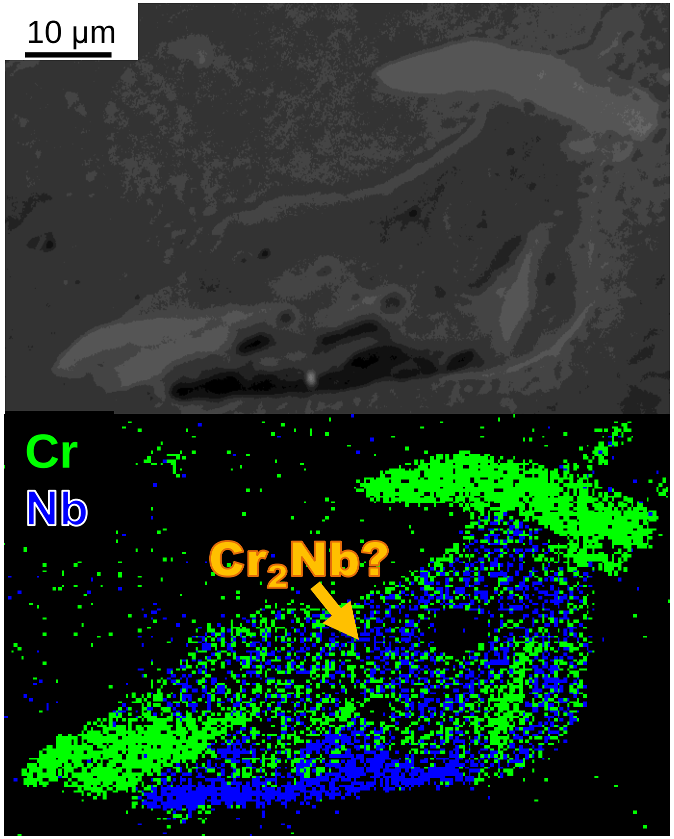
- Hatch spacing (72 µm) > Weld pool (56 µm)
  - Creates lack of fusion at any P-V combination



Printed Components

- In-situ alloying evident on metallographic sections.
  - Chromium (green) and niobium (blue).
  - EDS shows a mixture which suggests partially reacted Cr_2Nb
- Presence of Cr_2Nb not detected on XRD.
  - Cu peaks dominate XRD.
  - Cr_2Nb is below detection limit in bulk sample.



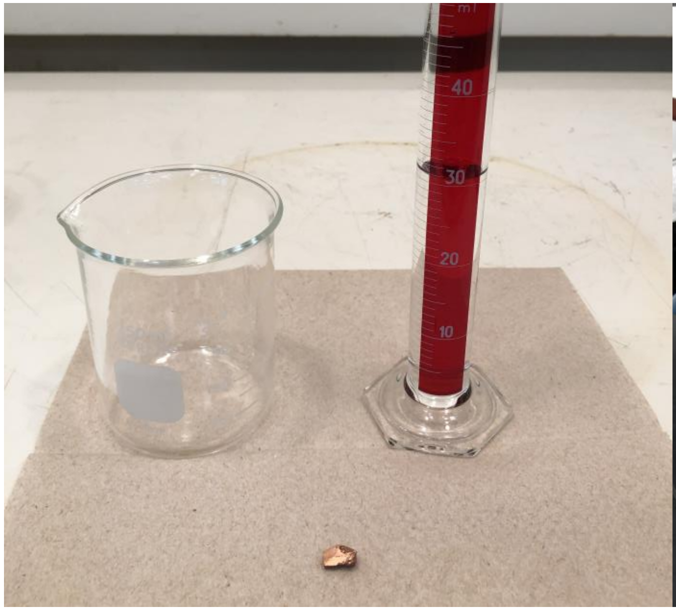


[4] D. Scannapieco, CWRU Senior Thesis, 2019.

Phase Extraction of Dispersoids

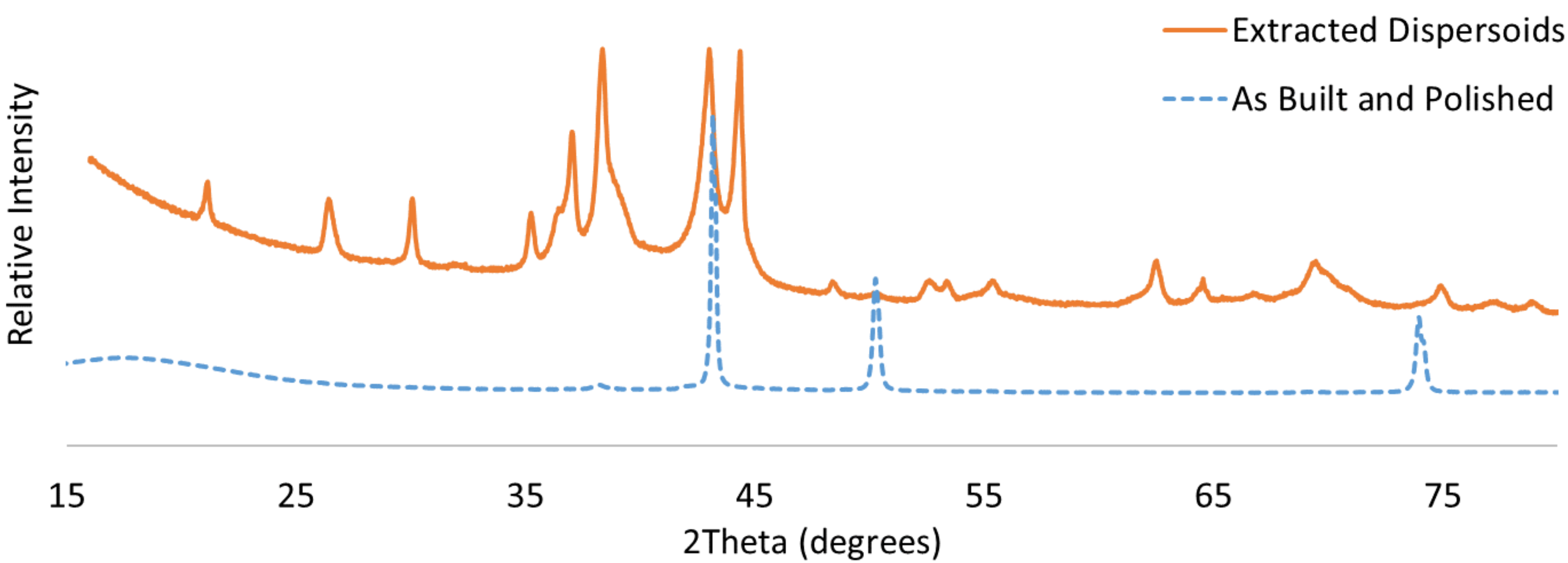
- To eliminate Cu from XRD consideration, extract out the Cr_2Nb dispersoids.
- Nitric acid is nonreactive with Cr, Nb, Cr_2Nb, and associated oxides.
  - Nitric Acid does dissolve Cu.

$$4HNO_3(l) + Cu(s) \rightarrow Cu(NO_3)_2(aq) + 2NO_2\ (g) + 2H_2O(l)$$



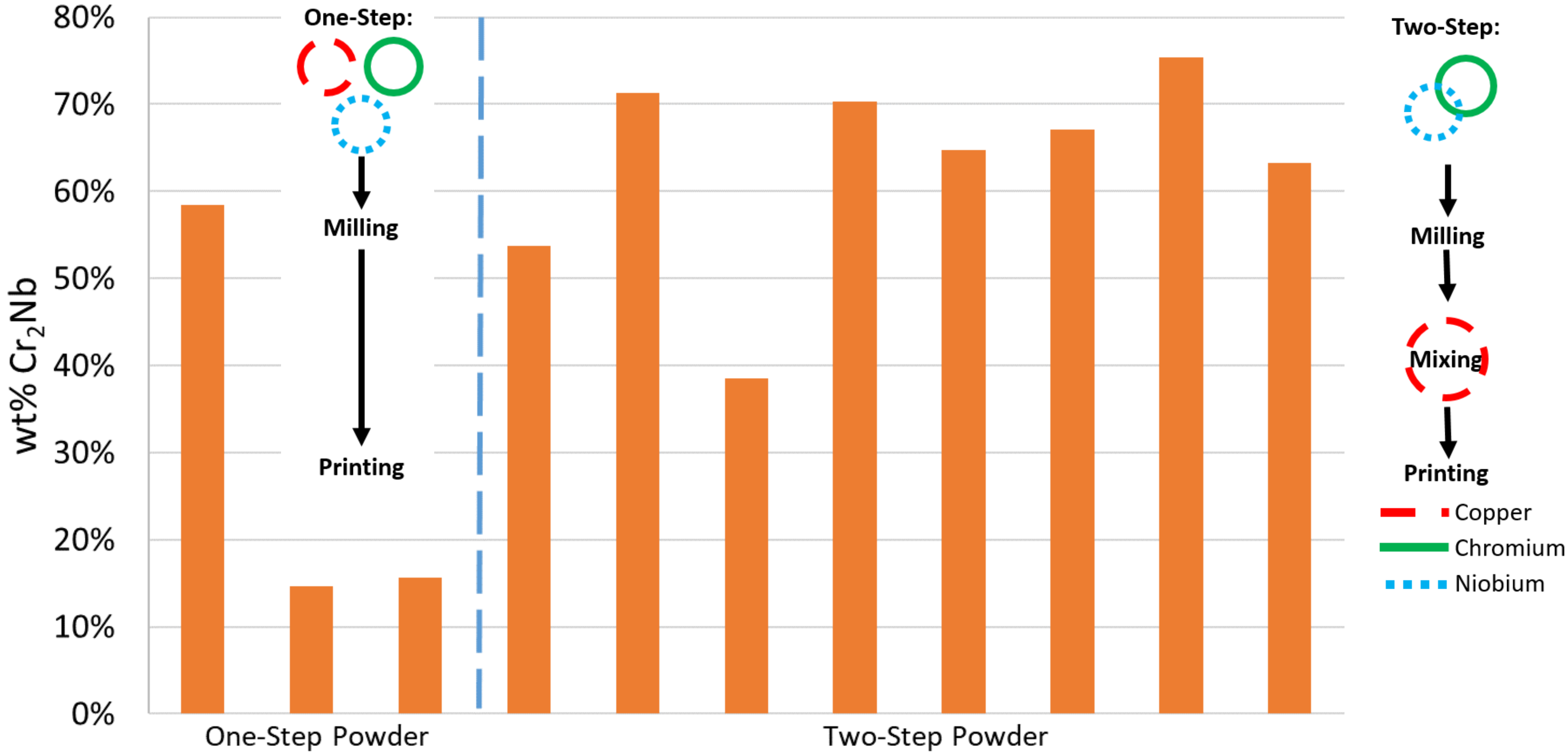
[5] L. Summerlin, et al., Amer. Chem. Soc. June 1987.

Phase Extraction of Dispersoid



- Phase extraction reveals presence of Cr_2Nb.
  - Dispersoids total 7 vol% of alloy.
- Can now identify differences in success of conversion to Cr_2Nb.

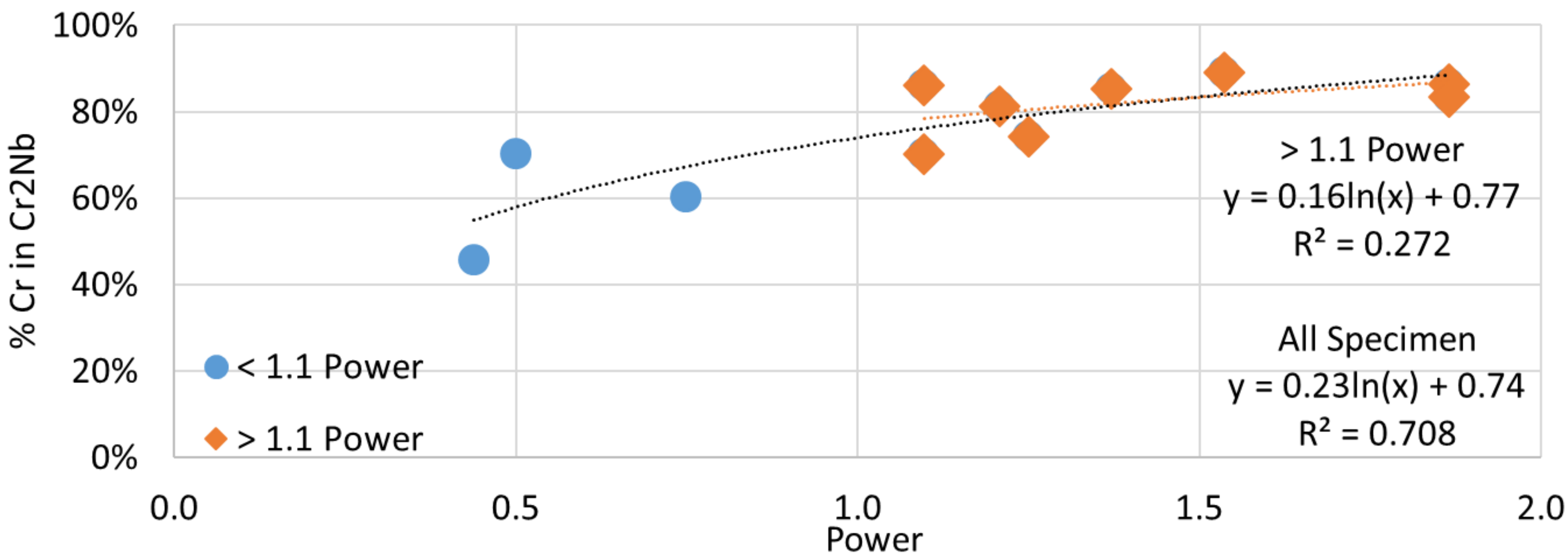
Milling Impact on Cr_2Nb Conversion



Two-step powder increases in situ formation of Cr_2Nb.

[6] D. Scannapieco, et al. NASA/TM-20205003857, June 2020.

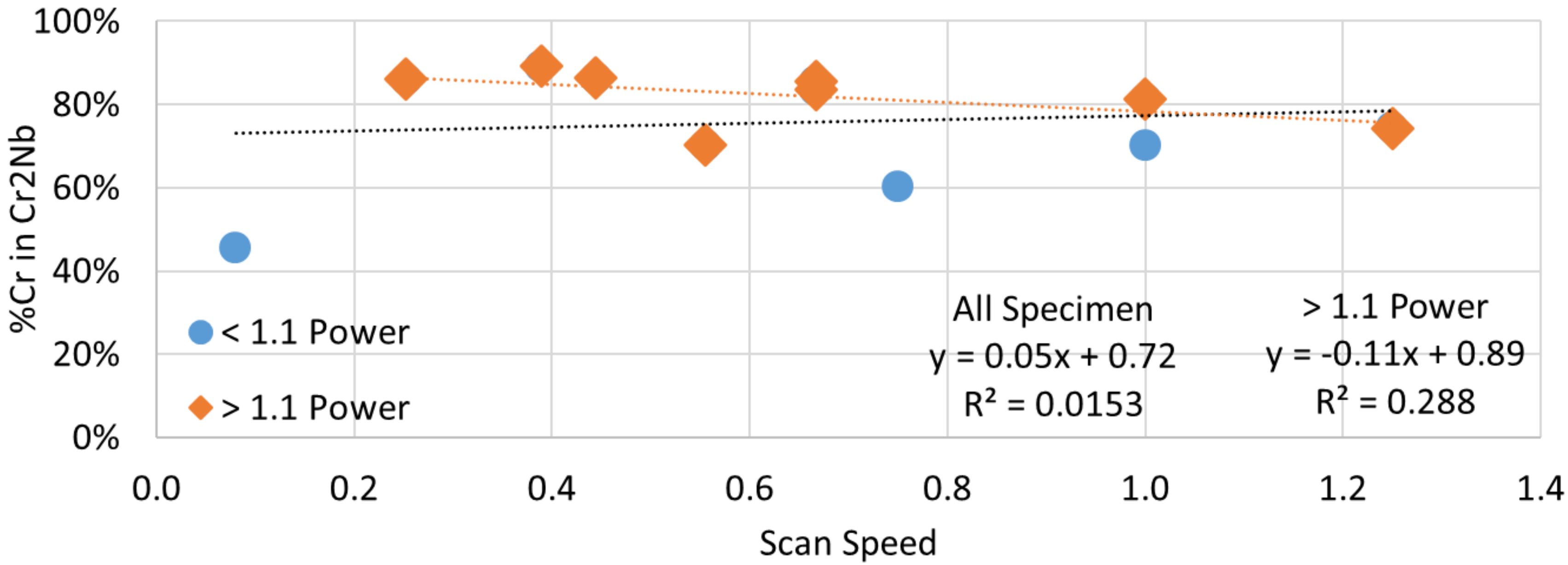
Laser Power Impact on Cr_2Nb Conversion



- %Cr in Cr_2Nb trends positively with Laser power.
- Clear distinction in laser power benefit above and below 1.1 power.
  - Suggests a minimum of 1.1 power is needed for high Cr_2Nb conversion.
  - Addition power above that is not an efficient means of promoting the reaction.

[6] D. Scannapieco, et al. NASA/TM-20205003857, June 2020.

Laser Scan Speed Impact on Cr_2Nb Conversion

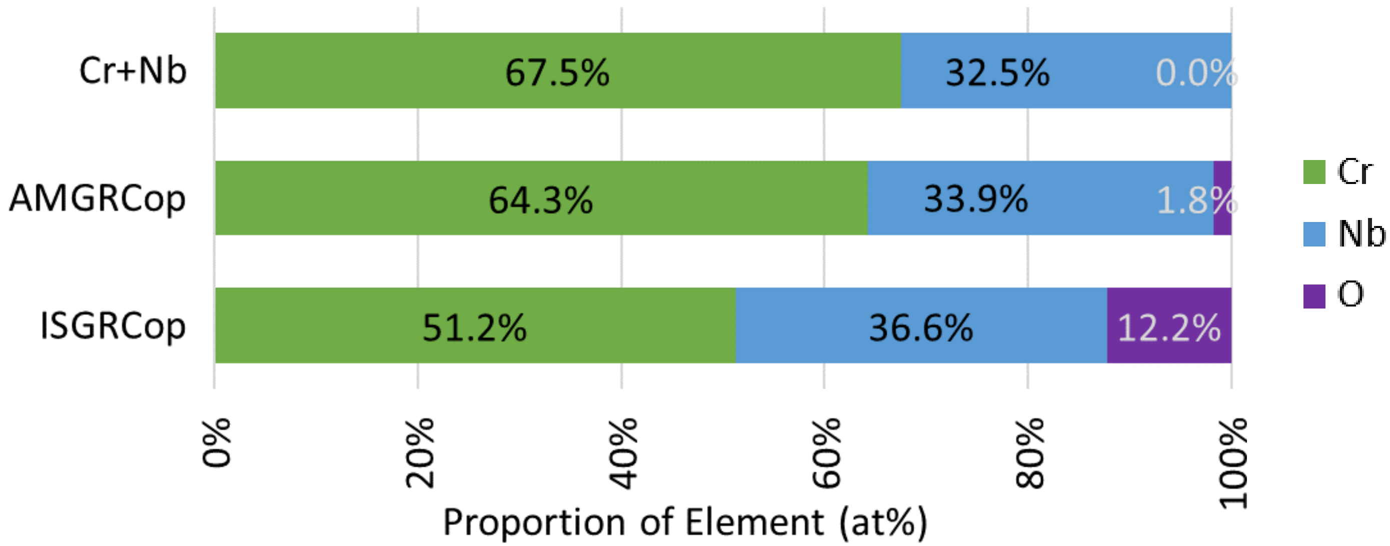


- Influence of scan speed on in-situ alloying success is negligible.

[6] D. Scannapieco, et al. NASA/TM-20205003857, June 2020.

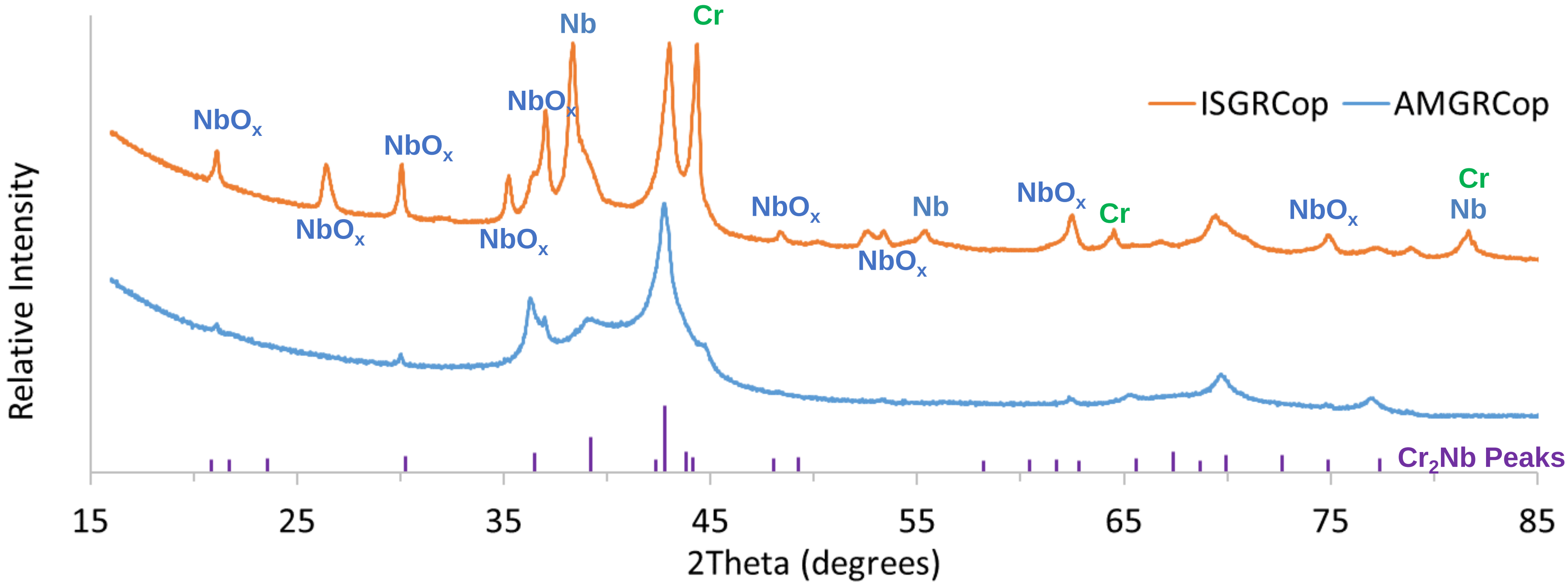
Processing Impact on Extracted Dispersoid Chemistry

- Powder (Cr+Nb) is oxygen free and Cr-rich, 2.08:1 Cr:Nb ratio.
- Both conventional AM and ISGRCop have oxygen, and are Nb-rich.
  - AM is 1.90:1 Cr:Nb ratio.
  - ISGRCop 1.40:1 Cr:Nb ratio, after starting with the 2.08:1 powder.
- No Oxides found in starting powders.



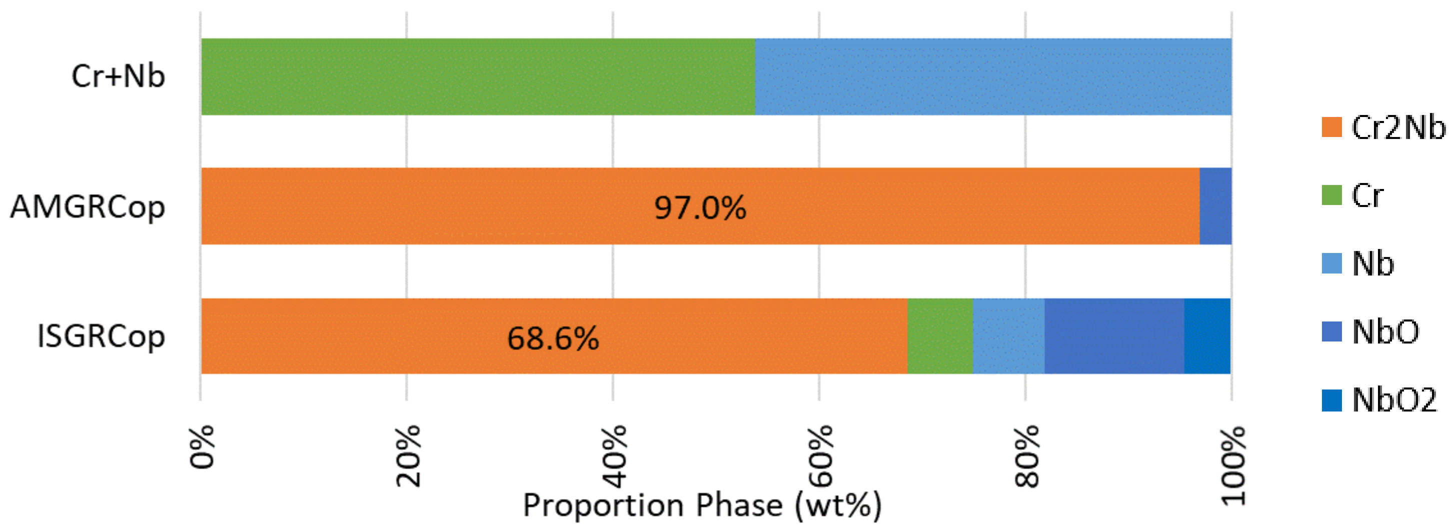
Processing Impact on Extracted Dispersoid Phases

- Extraneous peaks on ISGRCop line are primarily Nb-based oxides.
  - Very high oxygen content in ISGRCop dispersoids has an uncertain origin.
    - EOS M100 operates at < 0.1% Oxygen in the chamber.



Processing Impact on Extracted Dispersoid Phases

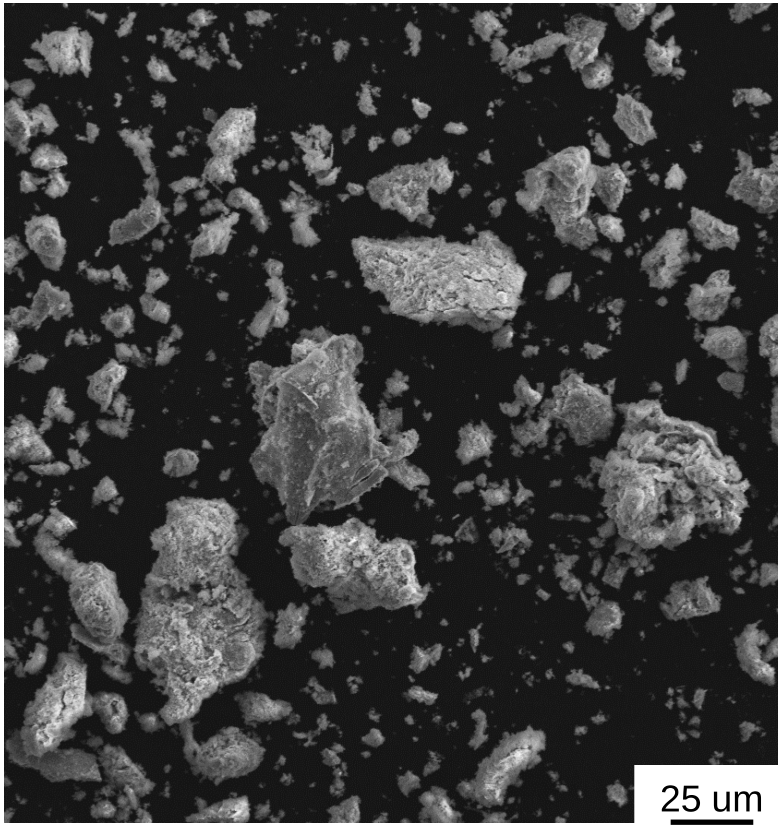
- ISGRCop remains well below reaction completion
  - Could be due to the hatch spacing issue, if the laser misses elemental powders they cannot react.
  - High O-content is in Nb-based oxides
- Oxides will continue to be monitored to identify their source.



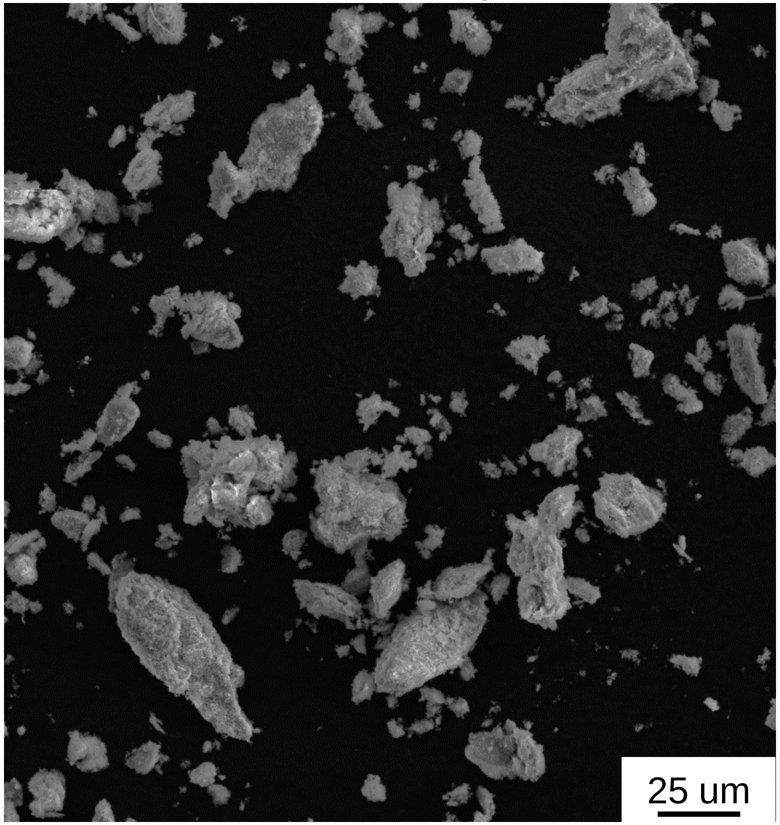
*AMGRCop contains two phases of Cr_2Nb

Processing Impact on Extracted Dispersoid Morphology

ISGRCop



AMGRCop



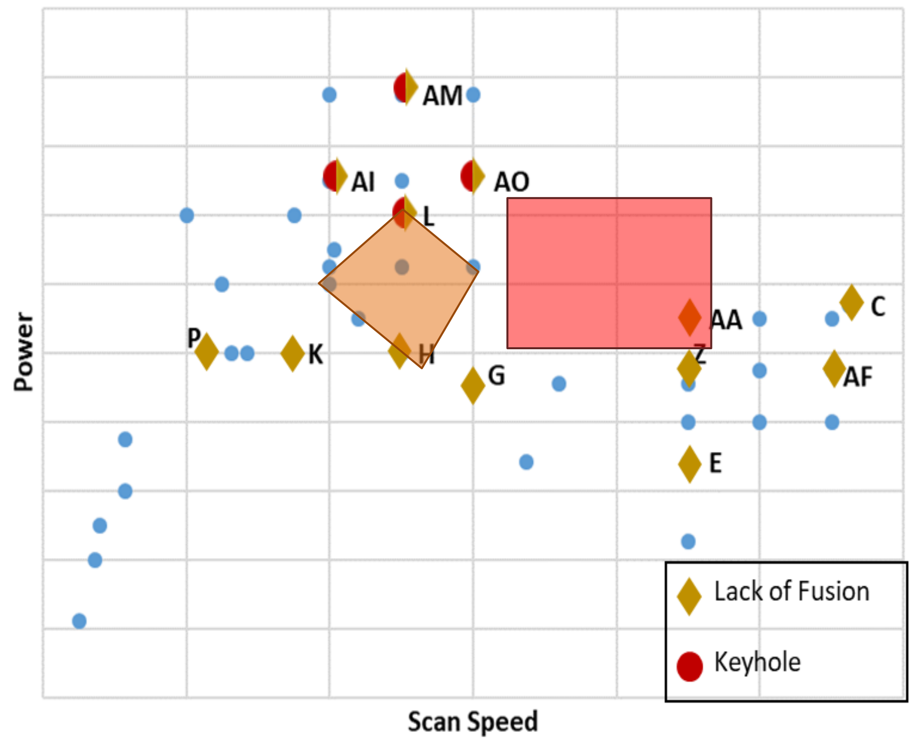
- Morphologies are similar between alloys.
- Suggesting that their mechanical strengthening effect will be similar.

Conclusions

- New in-situ alloying process during AM has been discovered for GRCop.
- Demonstrated feasibility of in-situ alloying for GRCop.
  - Possible and repeatable.
  - 80% conversion to Cr_2Nb with at least 1.1 normalized power.
- Able to react Cr and Nb to Cr_2Nb in the melt pool.
  - No alloy-related post processing needed, which may be required by other in-situ methods.
  - Extracted dispersoid morphology between gas atomized and AMed GRCop to the ISGRCop is very similar.
    - Promising for future mechanical properties.
- Only Nb-oxides were identified after print and extraction.
  - Could be fixed with better processing.
- Printing with elemental powders is not the same as with pre-alloyed powders, poses some development challenges.

Future Work

- Experiments to solve hatch spacing issue have been completed, evaluation is underway.
- Mechanical specimens have been built and will be tested to compare ISGRCop and AMGRCop.
  - Expectation is a similar mechanical performance.
  - Interest is in creep and fatigue particularly.
- This work has a US Patent Pending – LEW19909-1.



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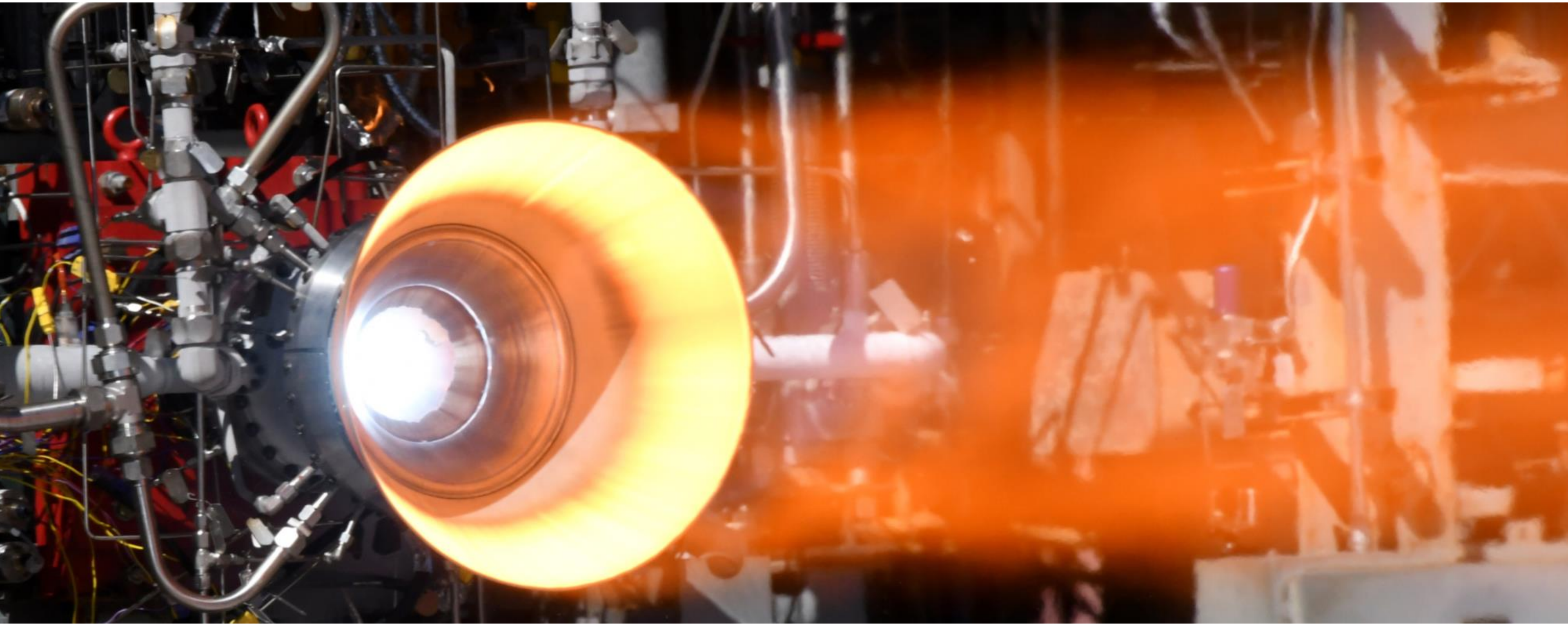

Questions?

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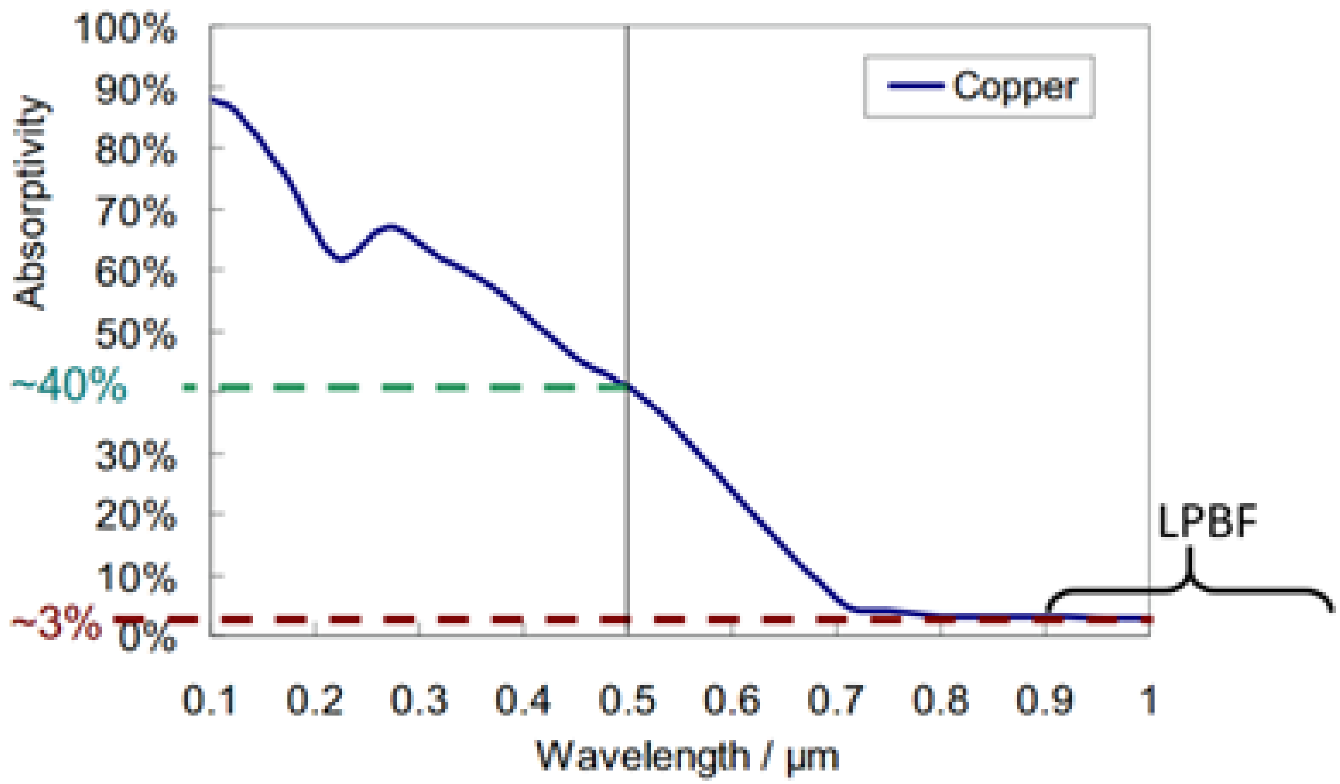
- Hess et al. Physics Procedia (2010).



Hess et al. Physics Procedia (2010)