# Additive Manufacturing of Carbon Nanotube Metal Matrix Composites


**Presenters:**

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**Navy STTR: N16A-T007**

**Army SBIR: A17A-033**

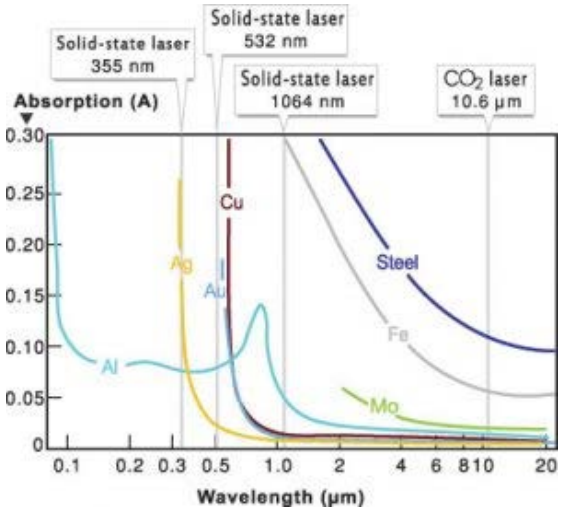
# Value Proposition

- Process to incorporate Carbon Nanotubes in to Powder Metal to:
  - Improve Stiffness and Strength through “long fiber” load transfer in a matrix
  - Reduce / eliminate thermal tear in non-eutectic alloys by forming nucleation sites
  - Improve laser power absorption by acting as surface coating to shift wavelength response


**2.5% vol Carbon Nanotube / 6061 Al produced on a Laser Powder Bed**

**Before Carbon Nanotubes**

**After mixing with Carbon Nanotubes**




**Carbon Nanotube absorption >0.97**



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# Takeaways

- Carbon nanotube metal matrix composites have been investigated through Navy STTR (17-4 stainless steel) and Army SBIR (aluminum) programs
  - Key threshold objectives were demonstrated in stiffness and strength improvements
- More research and development is required
  - Currently at TRL 3 / MRL 3
  - Utilized commercial raw materials and AM processing equipment
  - Entire process is industrial scalable
- Carbon nanotubes provide “long fiber” reinforcement within a metal matrix
  - Strengthening mechanism has been applied to other metal systems
  - Key is dispersion of the carbon nanotubes within the metal matrix



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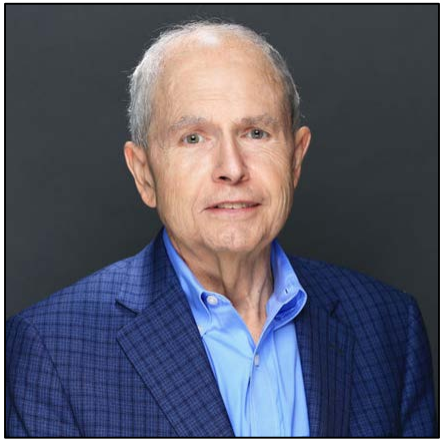
# UD-SHEPRA Project Team

**Robyn L. Bradford-Vialva**

**Fred Herman**



**Dr. Charles Browning**

**Dr. Li Cao**

**Dr. Don Klosterman**



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# Background Research

# Methodology

- Reviewed academic literature for peer reviewed work on carbon nanotube metal matrix composites
- Captured key performance metrics
  - Elastic Modulus
  - Yield Strength
  - Ultimate Tensile Strength
  - Strain to Fracture
- Tracked key input conditions
  - Matrix Material
  - Manufacturing Process
  - Mixing Process
  - Dispersion Quality
  - Carbide Formation
  - Volume Fraction of Carbon Nanotubes
- 41 different papers with 170 data points
- All data was normalized to reported control data

Table 1: Breakdown of Raw Data

| Matrix Material | Number of Papers | Number of Experimental Data Points |
|---|---|---|
| Aluminum (pure) | 18 | 61 |
| Aluminum Alloys | 10 | 48 |
| Titanium (pure) | 3 | 11 |
| Magnesium Alloys | 6 | 22 |
| Copper Alloys | 4 | 21 |



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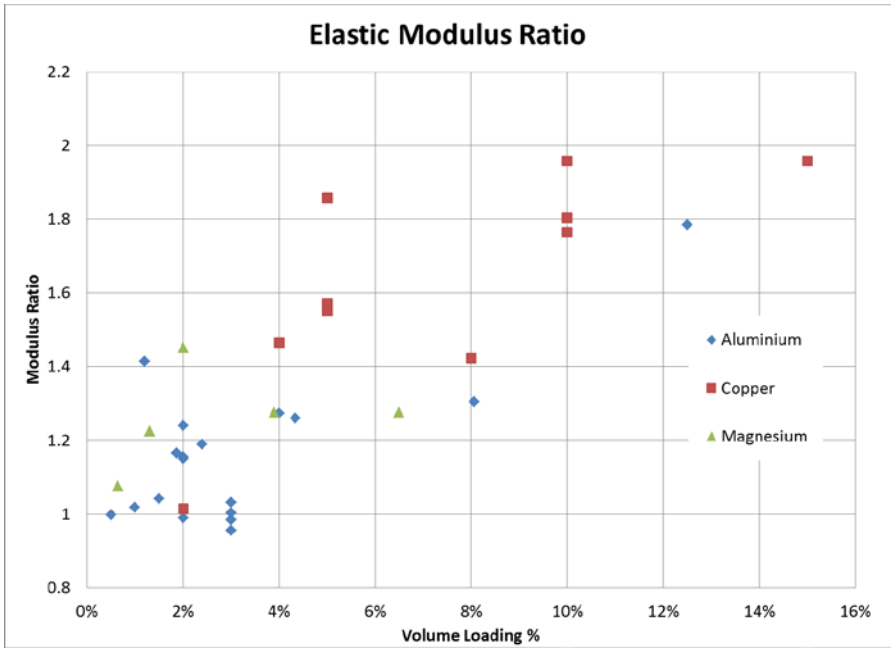
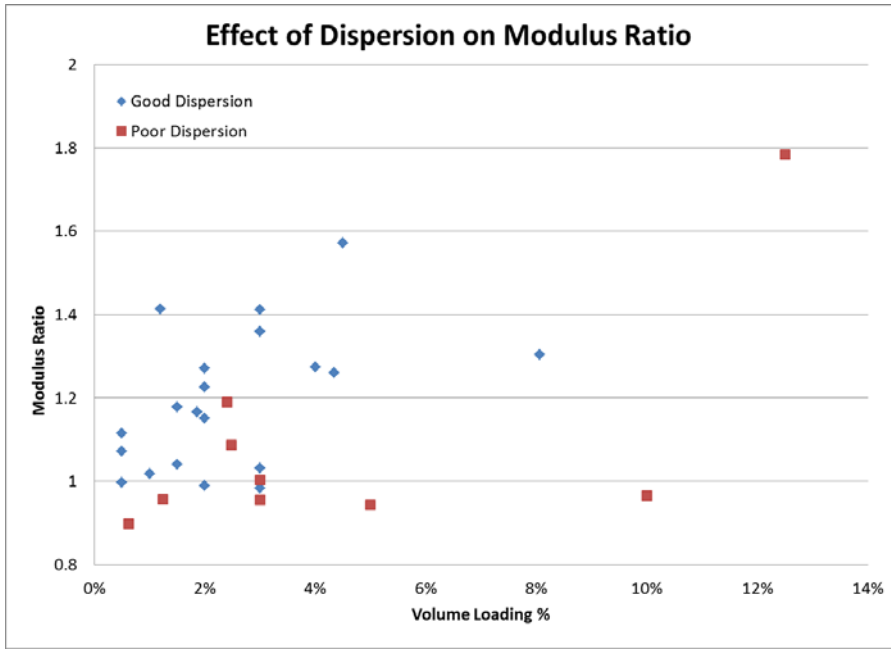
# Elastic Modulus Ratio




Positive trend between elastic modulus and volume loading

Trend applies to all metals

Good dispersion of carbon nanotubes results in statistically significant improvement in Elastic Modulus



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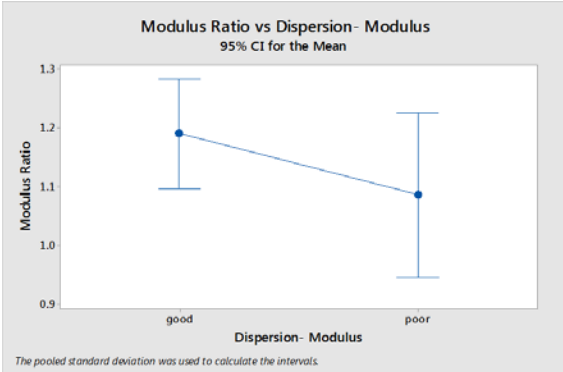
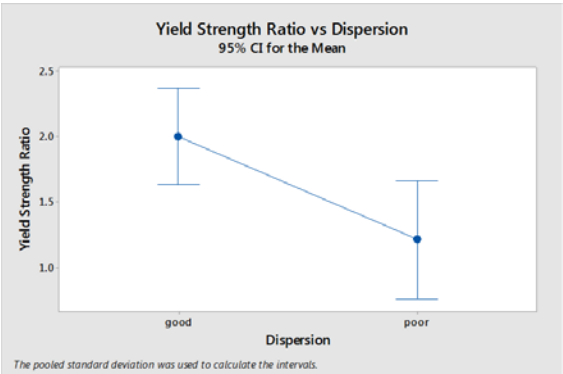
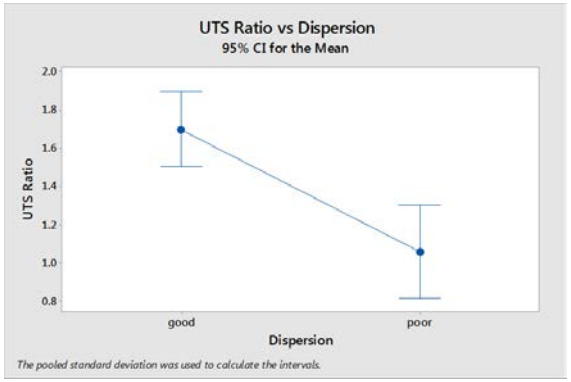
# Mechanical Properties vs. Dispersion




```
Analysis of Variance

Source                DF   Adj SS   Adj MS  F-Value  P-Value
Dispersion- Modulus    1  0.06806  0.06806     1.62    0.214
Error                 27  1.13308  0.04197
Total                 28  1.20114


Model Summary

        S   R-sq  R-sq(adj)  R-sq(pred)
0.204856  5.67%      2.17%       0.00%


Means

Dispersion-
Modulus        N    Mean   StDev       95% CI
good          20  1.1917  0.1662  (1.0977, 1.2857)
poor           9  1.0870  0.2757  (0.9469, 1.2271)

Pooled StDev = 0.204856
```




```
Analysis of Variance

Source          DF  Adj SS  Adj MS  F-Value  P-Value
Dispersion- YS   1   7.858   7.858     7.33    0.009
Error           51  54.637   1.071
Total           52  62.494


Model Summary

       S    R-sq  R-sq(adj)  R-sq(pred)
1.03504  12.57%     10.86%       6.75%


Means

Dispersion-
YS             N    Mean   StDev       95% CI
good          32   2.002   1.309  ( 1.635,  2.370)
poor          21  1.2151  0.2778  (0.7617, 1.6686)

Pooled StDev = 1.03504
```




```
Analysis of Variance

Source      DF  Adj SS  Adj MS  F-Value  P-Value
Dispersion   1   5.532  5.5323    16.62    0.000
Error       55  18.313  0.3330
Total       56  23.846


Model Summary

        S    R-sq  R-sq(adj)  R-sq(pred)
0.577035  23.20%     21.80%      18.38%


Means

Dispersion   N    Mean   StDev       95% CI
good        35   1.697   0.703  ( 1.501,  1.892)
poor        22  1.0567  0.2684  (0.8102, 1.3033)

Pooled StDev = 0.577035
```

Good dispersion versus bad dispersion analysis of variance (ANOVA) for:

- Modulus
- Yield Strength
- UTS

Multiple metal matrix materials

P-values

- Modulus: 0.214
- Yield Strength: 0.009
- Ultimate Tensile Strength: 0.000



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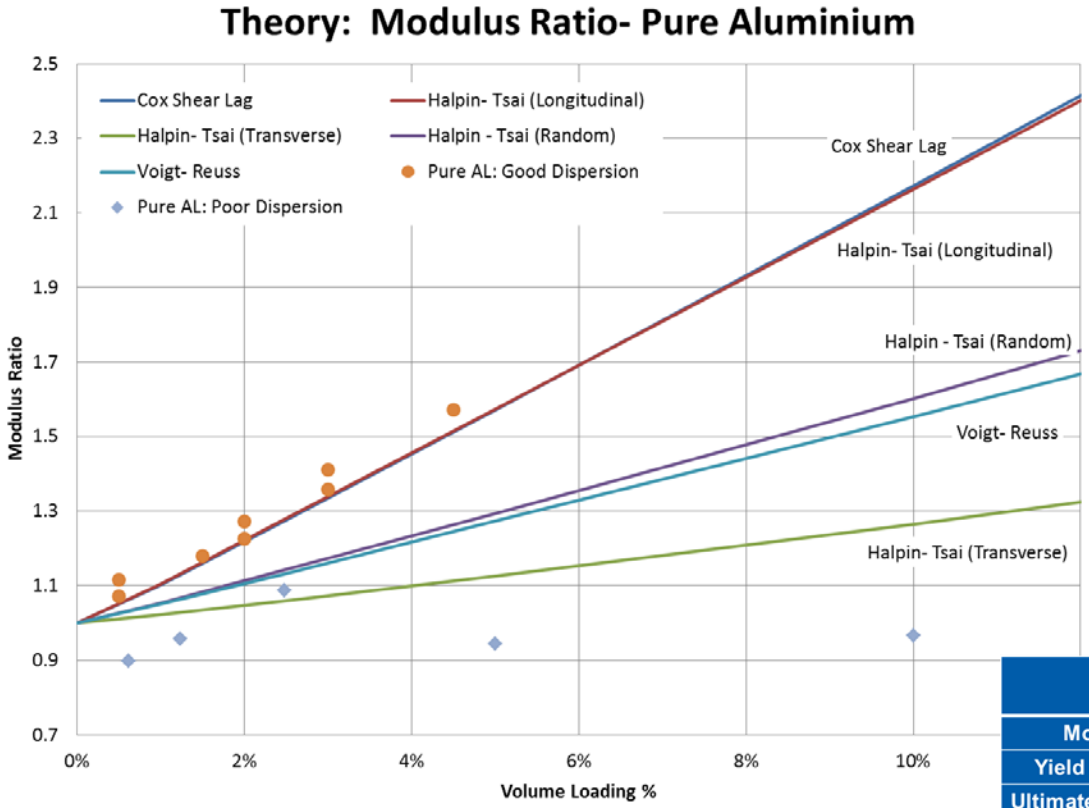
# Composite Theory vs. Modulus Ratio of Pure Aluminum




Comparison of various long fiber composite "rule of mixture" based models to published data for carbon nanotube/pure aluminum composites

| | Multiwalled Carbon Nanotube | 1050 – O Aluminum |
|---|---|---|
| Modulus (Gpa) | 1,000 | 70 |
| Yield Strength (Mpa) | -- | 28 |
| Ultimate Tensile Strength (Mpa) | 1000 | 76 |
| Shear Modulus (Gpa) | -- | 26 |
| Shear Strength (Mpa) | -- | 62 |
| Poisons Ratio | -- | .33 |
| Density (g/cm3) | 1.35 | 2.71 |
| Length (micron) | 5 | -- |
| Diameter (Nm) | 10 | -- |



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# Summation of Study Results

- Carbon nanotubes have successfully improved mechanical properties of multiple metal materials
- Mechanism is “long fiber” load transfer within the composite matrix
- Carbide formation was not a statically significant factor on modulus, yield strength or UTS
- Dry mixing or wet mixing techniques was best in achieving dispersion of the carbon nanotubes
  - Use of ionic processes or surfactants was not successful in achieving dispersion
- Powder consolidation process was not a factor as long as porosity was addressed



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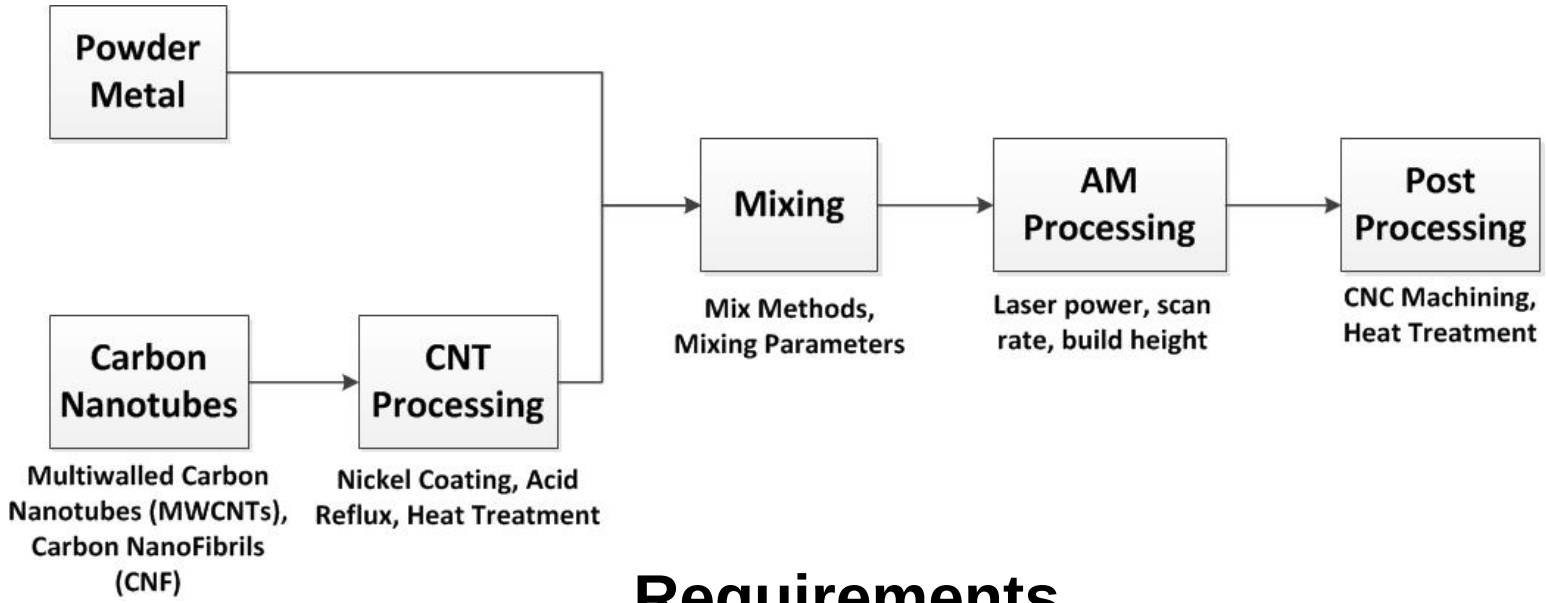
# Navy STTR Research

# Navy STTR Phase I / Phase I Option

## Baseline Process

**STTR: N16A-T007**

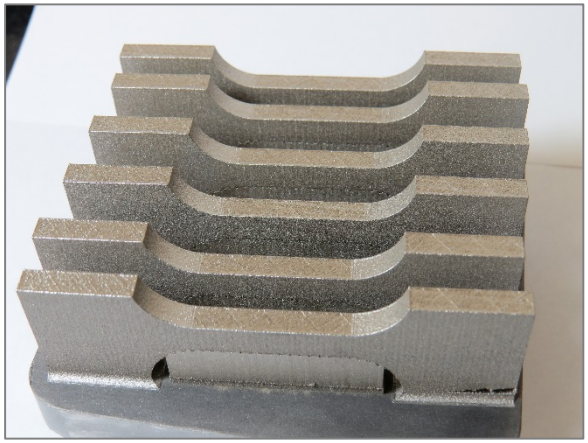



## Requirements

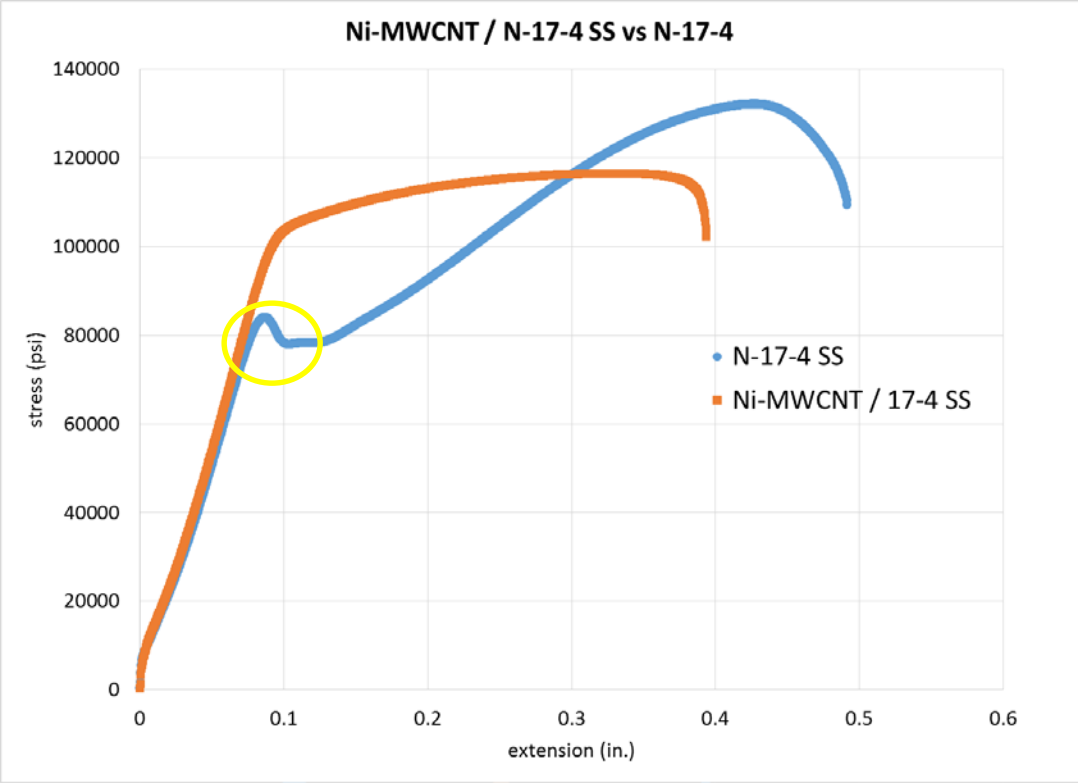
| | Heat Treatment | Yield Strength | Ultimate Strength | Hardness | Elongation |
|---|---|---|---|---|---|
| Threshold | H1025 | 145 Ksi | 155 Ksi | 35 HRC | 12% |
| Objective | H900 | 170 Ksi | 190 Ksi | 40 HRC | 12%* |

# Initial Results


MWCNTs / 17-4 SS



Ni-MWCNTs / 17-4 SS




- Use of Ni-MWCNTs eliminated the Lüders bands and increased yield strength by 20 Ksi
- Impurities in MWCNTs led to thermal tearing



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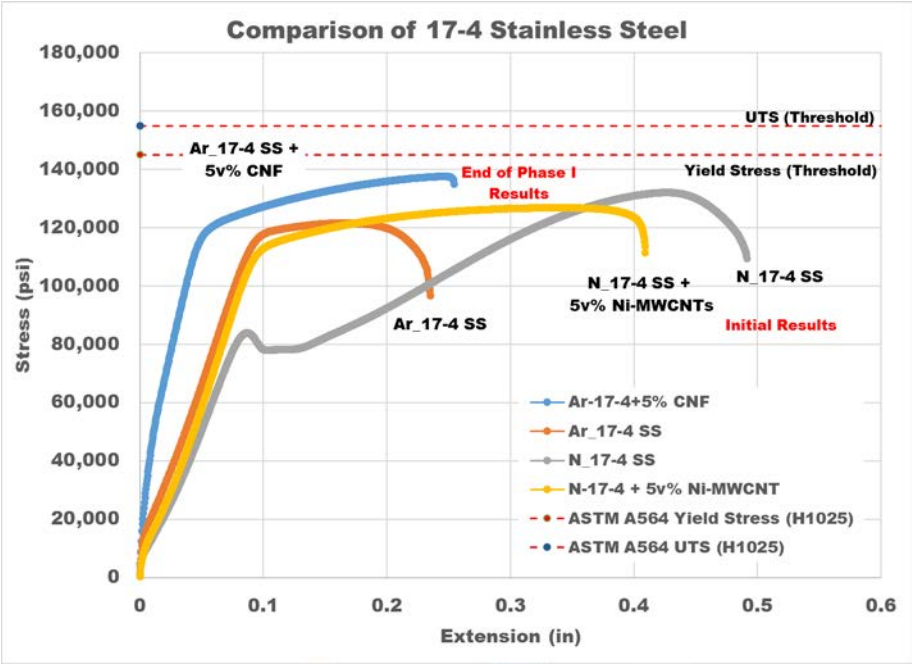
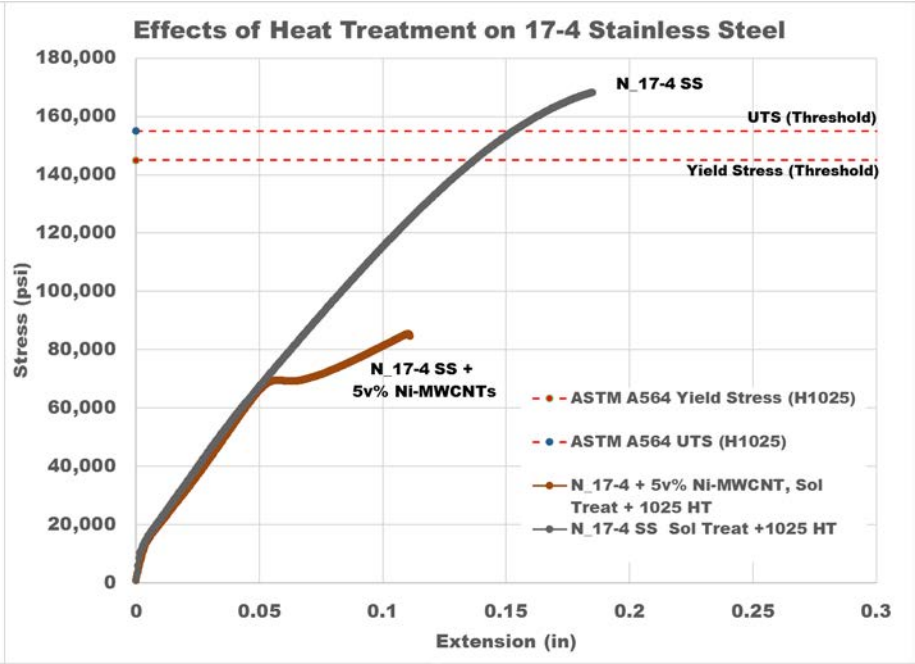
# Summary of Phase I Results




- Use of argon atomized 17-4 SS powder also eliminated Lüders bands
- Use of specially processed carbon nanofibrils (CNF) resolved thermal tearing issues and further improved mechanical properties
- Use of Solution Treatment and 1025 Heat Treatment achieved Threshold Requirements



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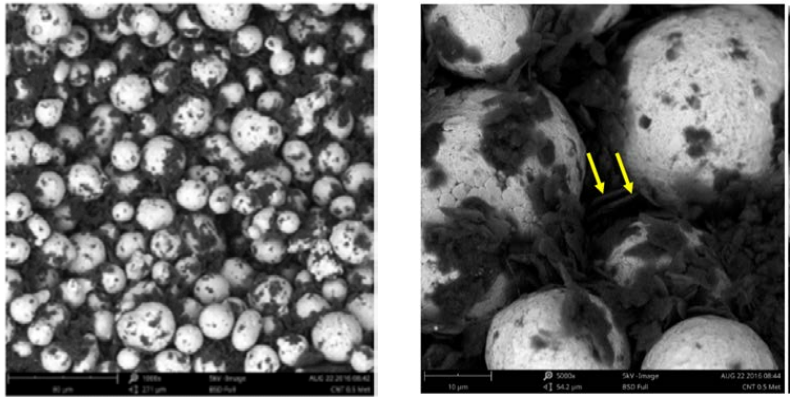
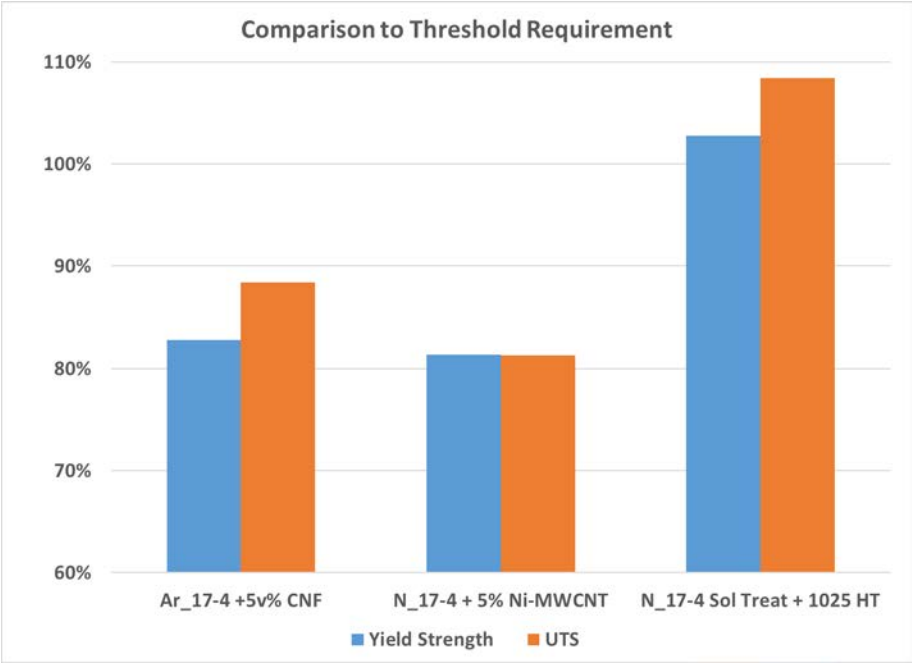
# Next Steps- Stainless Steel

- Leverage lessons learned from Army Phase I SBIR and apply to Navy Phase II STTR
  - Utilize special CNF processing on carbon nanotubes to prevent thermal tearing
  - AM processing parameters to decrease density
- Lessons learned from prior post-processing experiences
  - Machined surface finish required
  - Heat Treat using commercial processes



SEMs of dispersed Carbon Nanotubes



# Army SBIR Research

# Army SBIR Phase I

**Army SBIR: A17A-033**

- Leverage lessons learned from Navy STTR efforts
- Evaluated the use of lower cost aluminum (AlSi10Mg) metal powders
- Incorporate multiwalled carbon nanotubes
- Address porosity and thermal tearing issues that are inherent to AM processing of aluminum


1/3rd Section of 25 mm Sabot

| | Specific Modulus MSI/ lb/in$^3$ | Shear Strength KSI | Elongation | Cost |
|---|---|---|---|---|
| Threshold | 104 | 22 | 8% | 90% of current cost |
| Objective | 139 | 20 | 12% | 75% of current cost |



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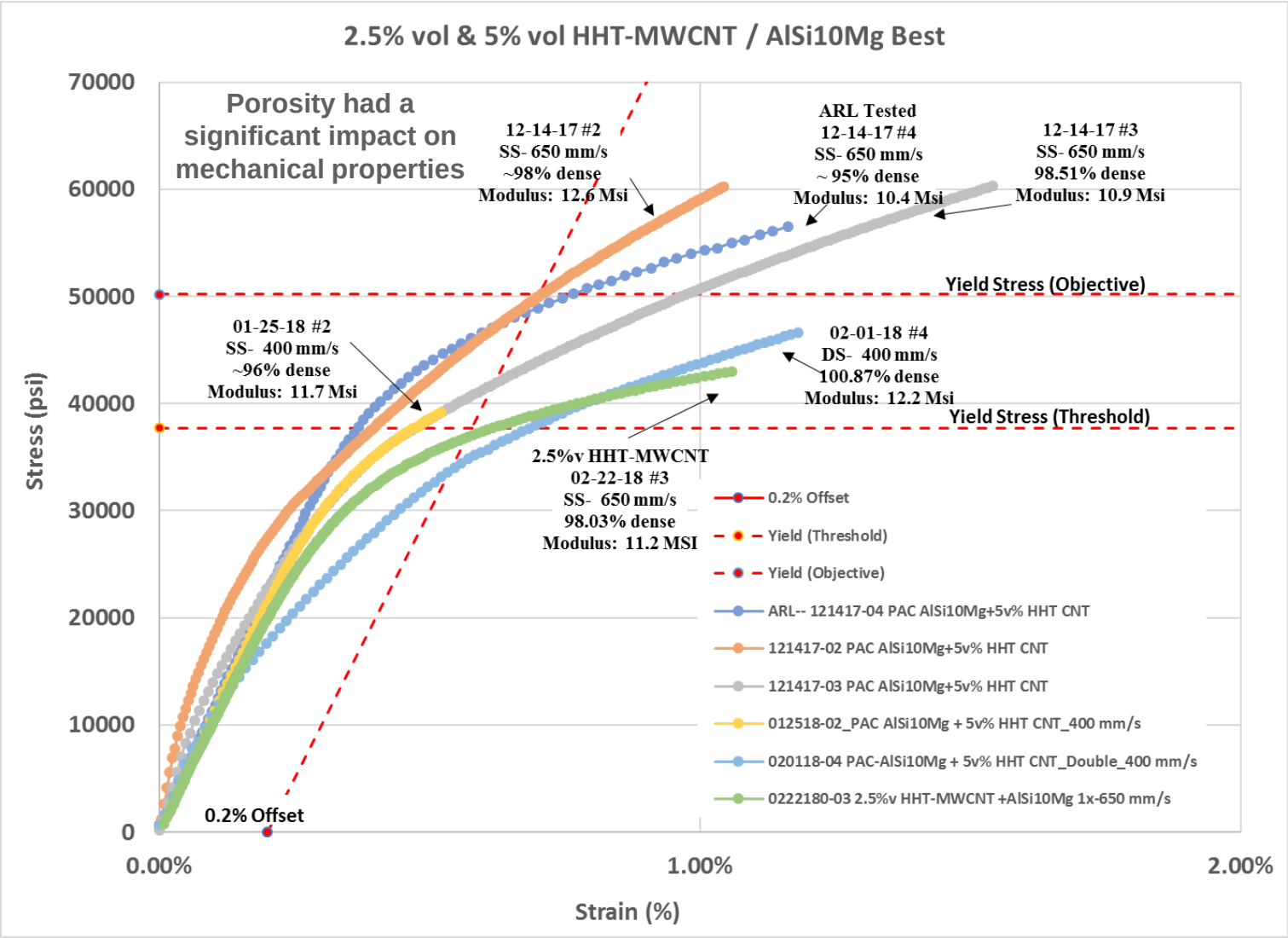
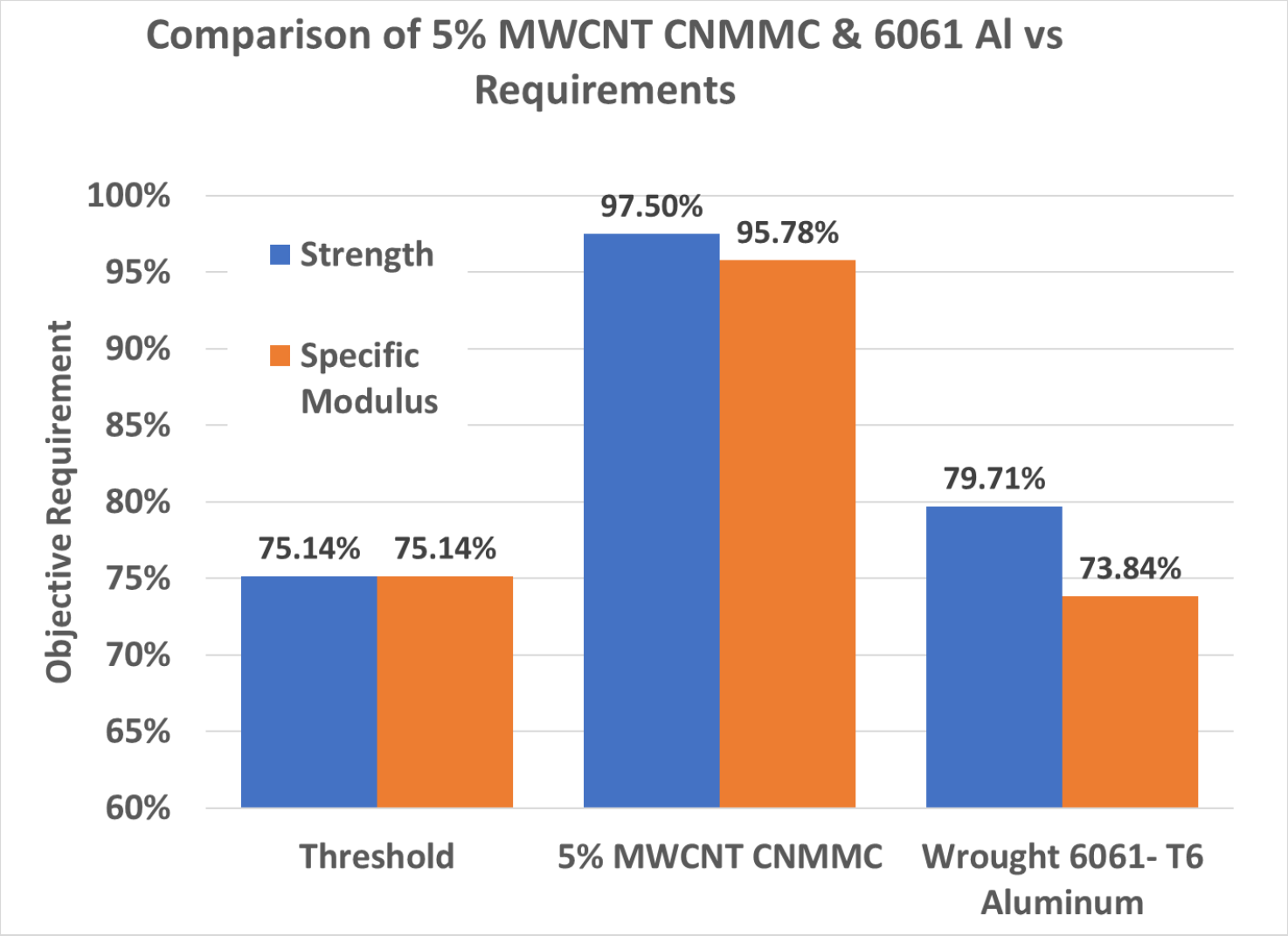
# Stress- Strain Curves for Aluminum



# Comparison to requirements & wrought 6061 Al



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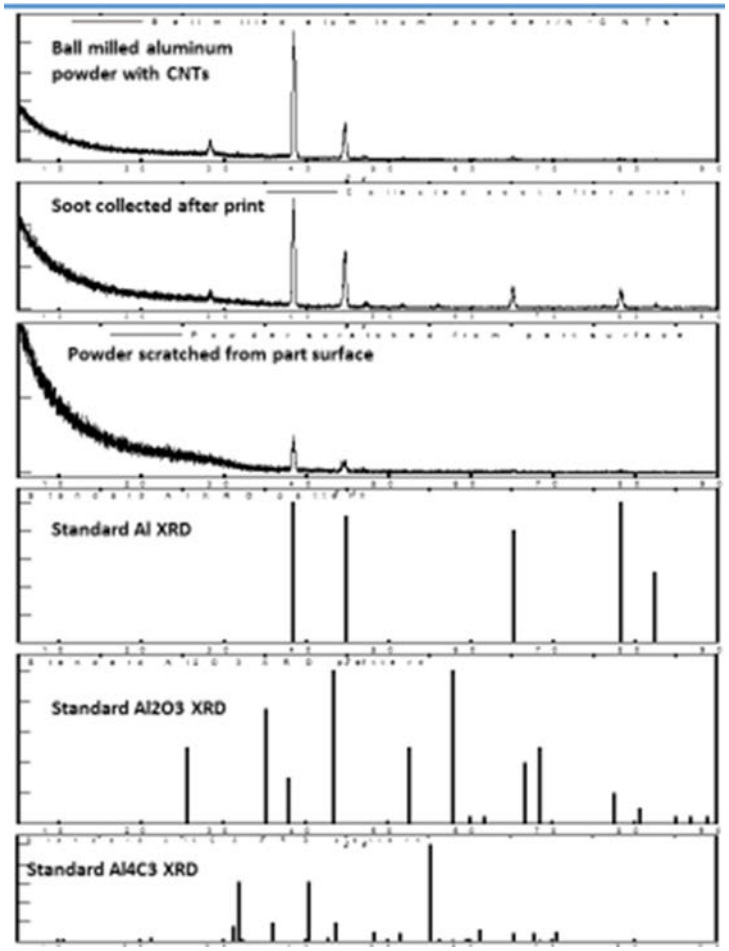
# Next Steps- Aluminum

- Army phase II SBIR proposal submitted March 2018
- Porosity had a significant impact on mechanical properties, especially elongation to failure
- Address porosity through the following:
  - Adjust powder size and morphology to improve re-coating
  - Optimize build height, laser power, laser scan rate and number of laser scans
- Carbide formation and carbon nanotube thermal tear issues have been addressed
- Carbon nanotubes act as nucleation sites in the melt pool look at other aluminum alloy and metals




**X-ray diffraction shows no formation of Aluminum Carbide or Aluminum Oxide**



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# Conclusions

- Carbon nanotubes have demonstrate improve strength and stiffness in aluminum (AlSi10Mg) and 17-4 Stainless Steel
- Carbon nanotubes has been applied to strengthen & stiffen other metal systems
  - Key to success is dispersion
- More research and development is required
  - Currently at a TRL 3 / MRL 3
  - Utilized commercially purchased raw materials and AM processing equipment, Entire process is industrial scalable
  - Should Cost modeling indicates Army cost requirements can be met



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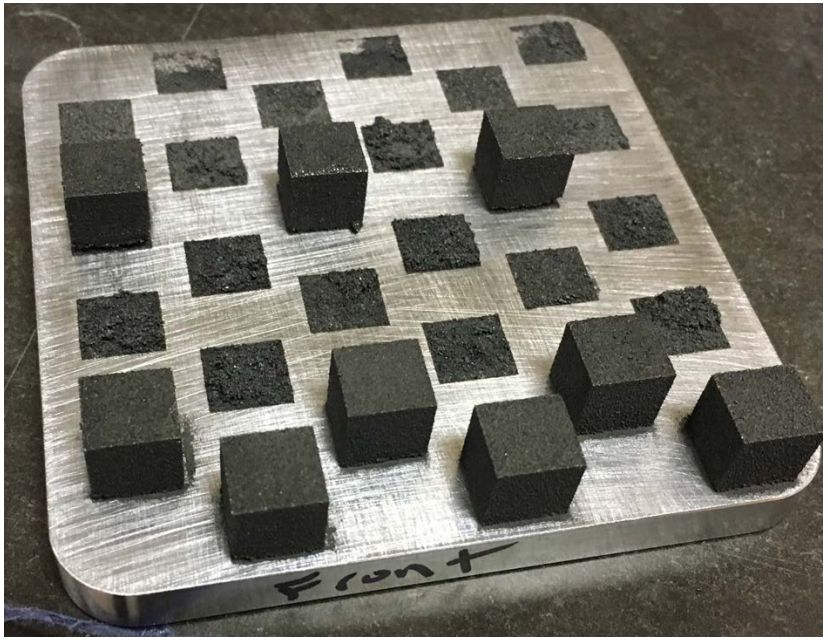
# 6061 Aluminum

# Initial 6061 Trials





Initial Design of Experiments Trial On AM Processing Parameters

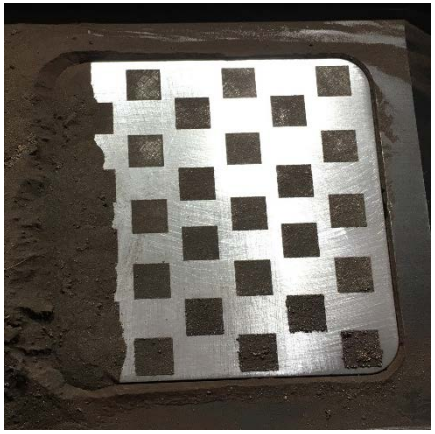
3 of 9 processing parameter sets were successful

Second batch of 6061 specimens using best available AM processing parameters

Wire brushed to remove top layer of unmelted metal powder

# Copper

# Initial Copper Trial



Used same DOE parameters as 6061 Al trial

Initial layers did not stick to the build plate

Subsequent layers were melted but swept aside by the re-coater blade.

Laser at max powder (95W), more laser power and additional laser scans per layers might be beneficial



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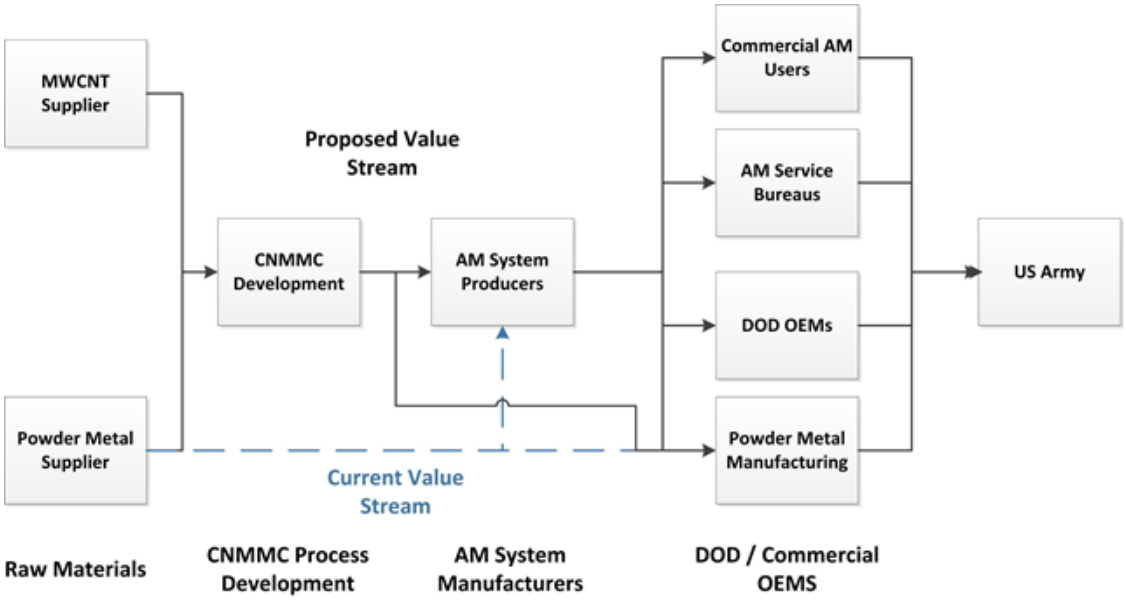
# Commercialization plan

# Commercialization Plan




Core Technology is applicable to other Powder Metallurgy manufacturing processes such as die cast, metal injection molding.

Current Status:
TRL / MRL: 3

- Multiple commercial materials suppliers for raw materials
- Work with DOD services / DOD OEMs to establish “tech pull”
- Co-develop and license to AM system manufacturers and powder metal suppliers to establish sales channel



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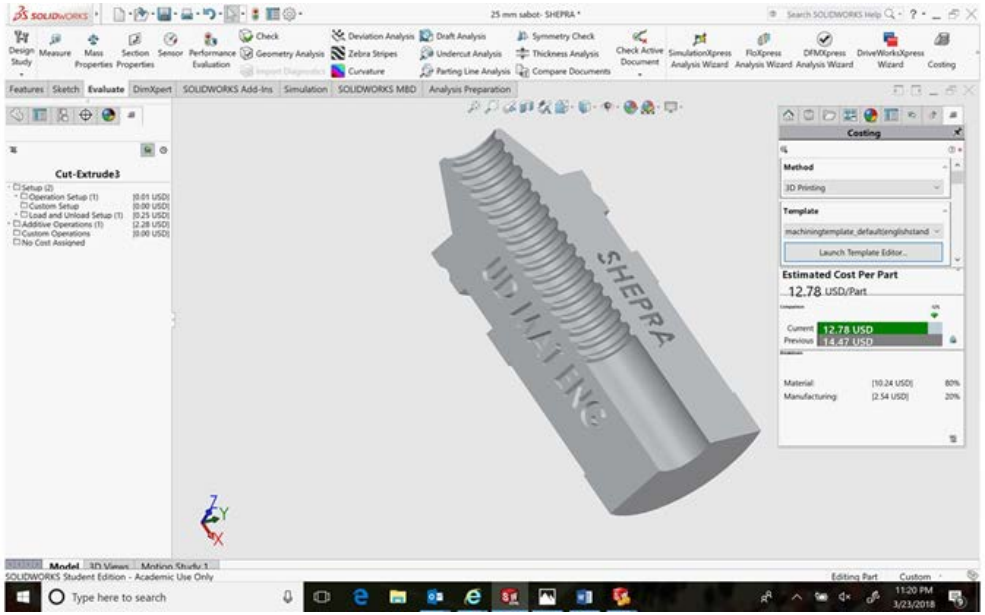
# Should Cost Modeling




**"Should Cost" modeling performed on SolidWorks**

| Manufacturing Process | Raw Material | Material Cost | Labor & Operations Cost | Tooling | Total |
|---|---|---|---|---|---|
| CNC Machining | 6061 Al-T6 | $0.34 | $8.54 | $0.00 | $8.88 |
| Additive Manufacturing | 2.5% MWCNT | $1.20 | $2.55 | $0.00 | $3.75 |
| Die Cast | 2.5% MWCNT | $1.05 | $3.40 | $0.50 | $4.95 |

**Machined 6061 Al does not meet performance requirements**

* Price for laboratory quantity

| Raw Material Cost | | |
|---|---|---|
| | Density ($g/cm^3$) | $/Kg |
| AlSi10Mg Powder | 2.68 | $55 |
| MWCNT + Processing | 1.5 | $242* |
| 2.5% MWCNT / AlSi10Mg | 2.65 | $59.07 |
| 5% MWCNT / AlSi10Mg | 2.62 | $63.25 |

- Use of Carbon Nanotubes not a significant cost increase
- TPOC validated, results are consistent with current production cost of sabots
- Some additional post-processing is required for AM



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# Current Status / Next Steps

## Current Status

- Navy STTR (17-4 SS): Passed DCAA audit, NAVAIR KO finalizing contract for phase II
- Army SBIR (aluminum): Submitted phase II proposal (3/30/18), surpassed 3 of 4 threshold requirements.

## Next Steps

- Identify potential applications (DOD / commercial)
- Mix, Melt and Test
- Identify additional funding opportunities
- Look at additional metal alloys