Nanostructured Alloys as an Alternative to Copper-Beryllium

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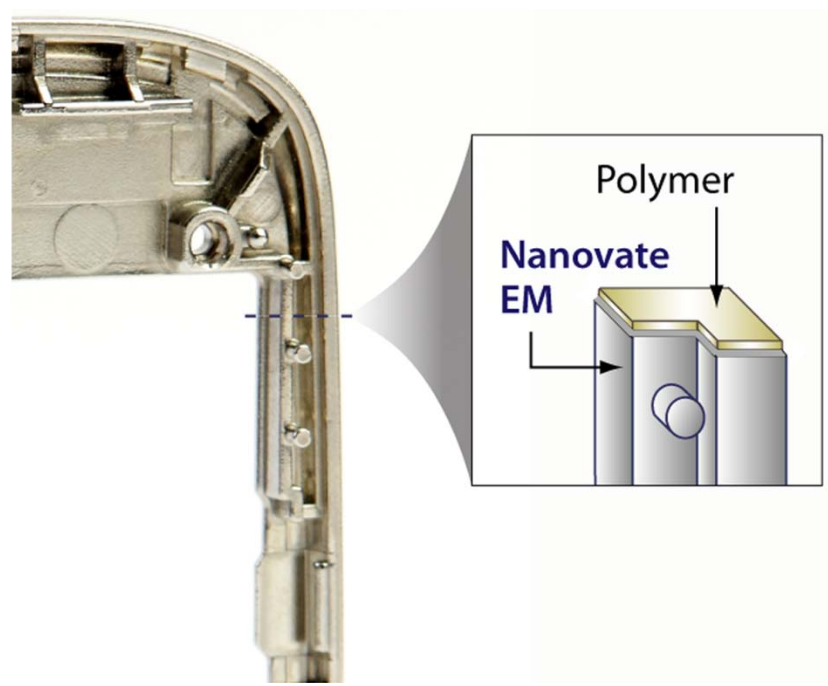
Advanced Materials

Integran Technologies provides innovation solutions to the material selection process to improve performance and decrease weight based on our **Structural** and **Functional** Nanometal coatings and electroforms.

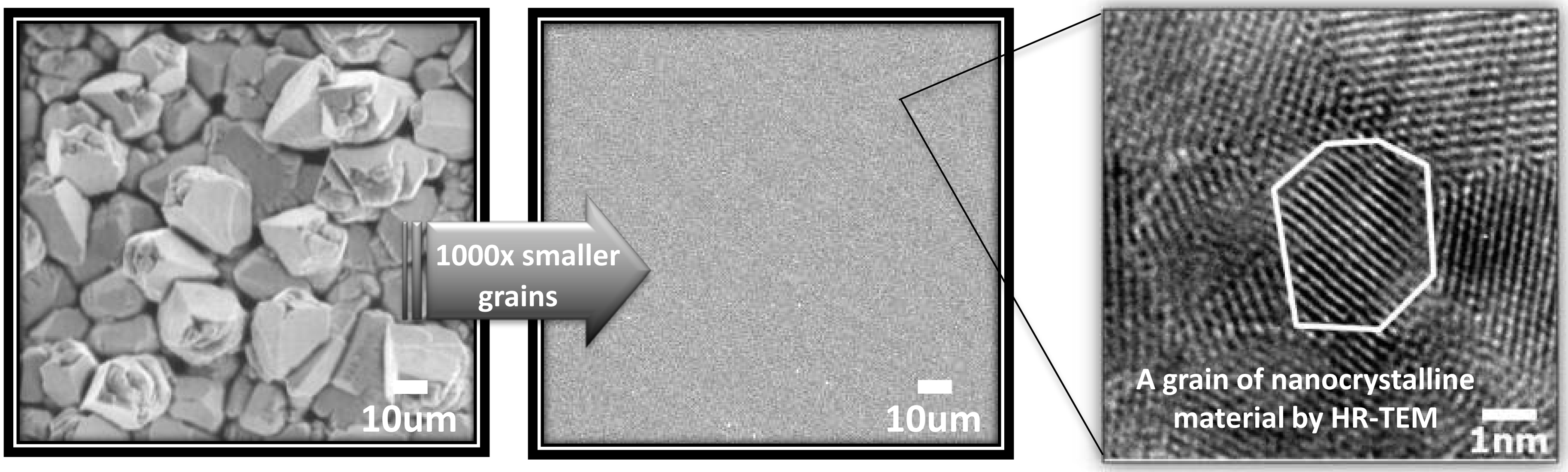
Structural – High strength / stiffness / toughening structural reinforcement of aluminum, polymers and composites or bulk electroforms.

Functional – High wear resistance, low friction, anti-galling, low erosion, corrosion protection, magnetic shielding, electrical conductivity.



What is a Nanostructured Metal?

Conventional Metals | **Nanovate™ Metals**



Grain size = 10 – 100um | **Grain size = ≤ 20 nm**

A Nanostructured Metal is simple a metal with an average grain size in the nanometer range (10-100nm) compared to >1µm for a conventional metal

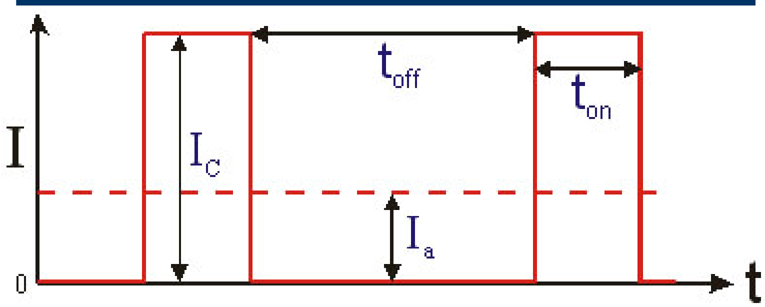
Decreasing Grain Size Dramatically Improves Hardness and Strength

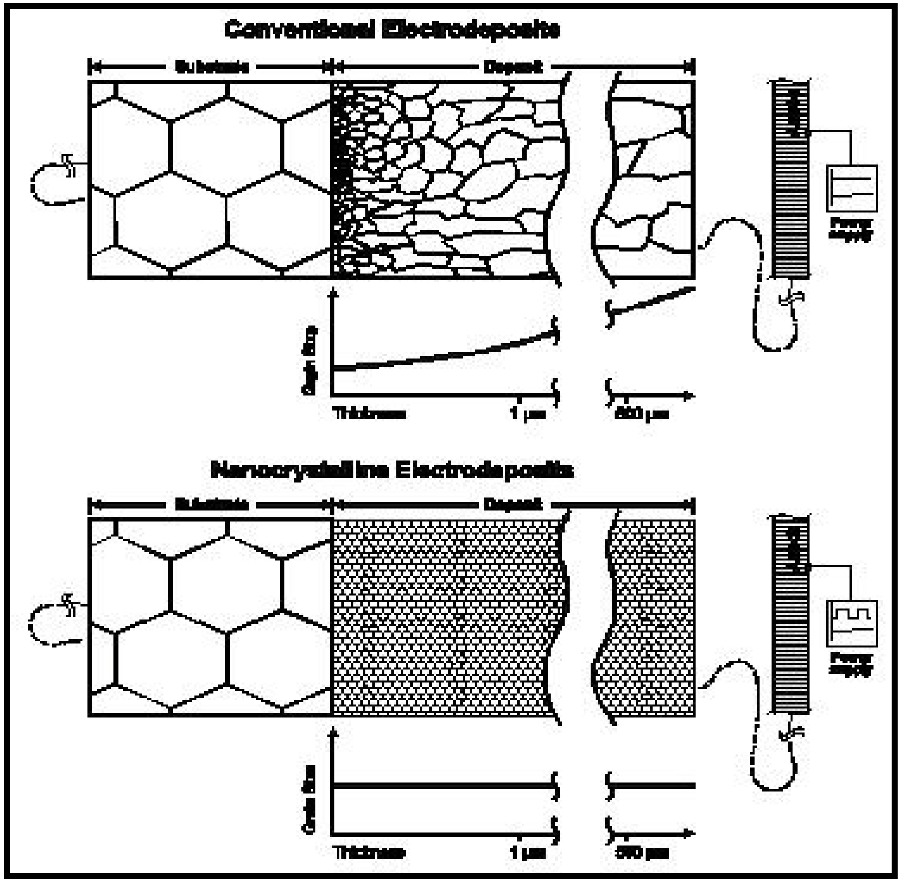
Property	Units	Conventional Ni (20 um)	Nanovate Ni (20 nm)
Yield Strength	MPa	100	900
Ult.Tensile Strength	MPa	400	1400
Vickers Hardness	kg/mm^2	140	450

How do we achieve unique properties?

Microstructural Control by Pulsed Electrodeposition

Pulse Plating favors nucleation of new grains over growth of existing grains, resulting in an ultra-fine grain structure throughout the entire thickness of the coating, right from the substrate interface.





Pulsed Electrodeposition from Aqueous solutions results in the deposition of fully dense metal with a nanocrystalline grain size. At **no point** in the fabrication process are nanosized powders produced.

Several Nanovate™ Alloys Available

N1000 Series - *Nickel*

Good hardness, wear, and corrosion resistance as well as good strength properties. Also used for erosion protection of composites.

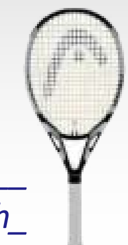
Grafalloy Epic™ golf shaft - graphite/epoxy coated with Nanovate™ N1010

N2000 Series – *Nickel Alloy*

Higher strength than the N1000 series. Some compositions also offer magnetic shielding properties, increased resilience, or decreased CTE.

EMI shielded cell phone casing

Metallix™ HEAD racquet with Nanovate™ N2015 foil



R3000 Series - *Cobalt*

Superior hardness, wear, and corrosion resistance; it has been validated as an environmentally friendly alternative to hard chrome. Also has excellent structural properties.

Nanovate™ R3010 for hydraulic actuators

C4000 Series – *Copper*

Strong and hard, fine grained Cu being developed for electronics, high strength wires, anti-microbial and defense applications.

Nanovate™ C4010 shape charge liner

Problem Statement

The Benefits of Copper Beryllium

- Cu-Be is the **hardest** and **strongest** of any copper alloy.
- The high yield **strength** and high **stiffness** make it an ideal material for components under repeated stress and strain (spring wire, load cells, bushings, etc).
- Other advantageous properties include: good conductivity, low friction, non-galling, non-sparking, nonmagnetic, good high temperature and corrosion resistance.

The Drawbacks of Beryllium Copper

- Exposure to Be results in a range of diseases including lung cancer and Chronic Beryllium Disease (CBD).
- DoD employees are exposed to Be dust and fumes as a result of the wearing of Be-containing alloys during operation and during machining and other fabrication operations
- An **environmentally benign alternative** is required for worker health and safety

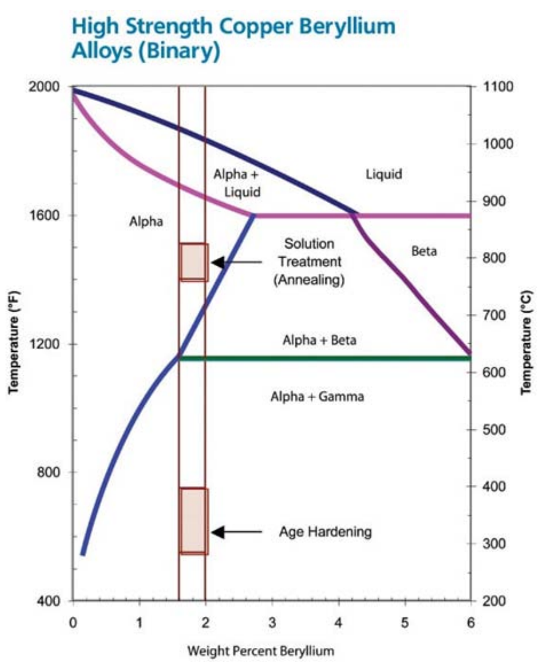
Technical Objective of SERDP

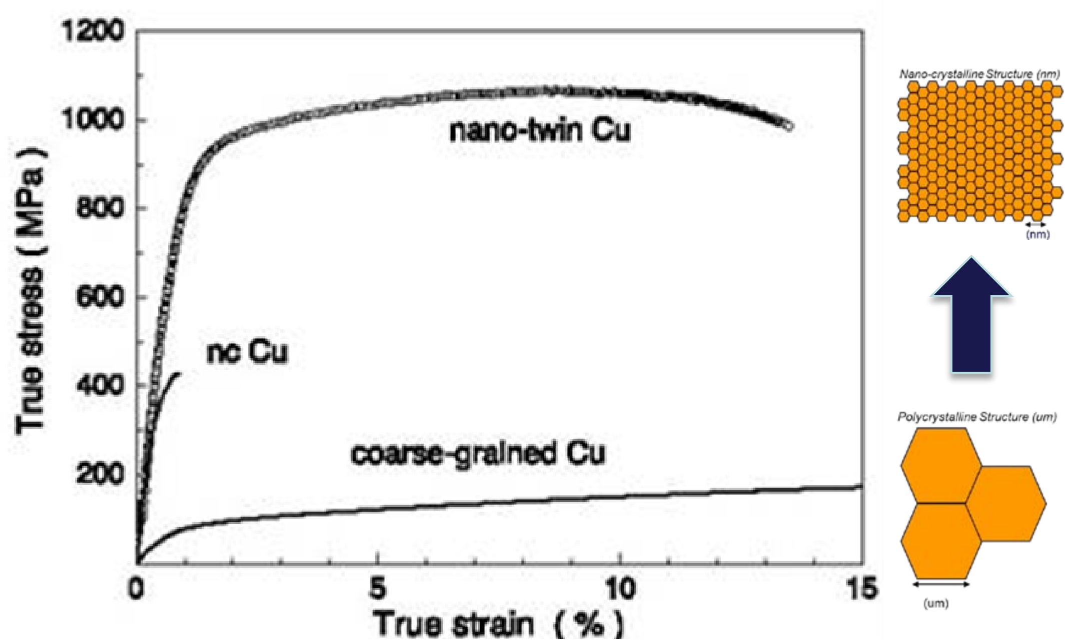
- Develop and validate a cost-effective and robust nanocrystalline alloy electroplating/electroforming process that is capable of producing material that conforms to property requirements for current and future copper-beryllium alloy needs/ applications

- Demonstrate with three distinct product forms:
  - ♦ **1) Bulk material for bushing applications;**
  - ♦ 2) Nanometal/composite for high specific strength/stiffness components; and
  - ♦ 3) Nanometal cobalt/copper enabled conductor wire

Technical Approach

- **Instead of employing age hardening with beryllium bearing copper alloys (or work hardening with current CuBe alternatives), Integran will improve the properties of copper alloys through grain size reduction / refinement to the nanostructured regime**





Technical Approach

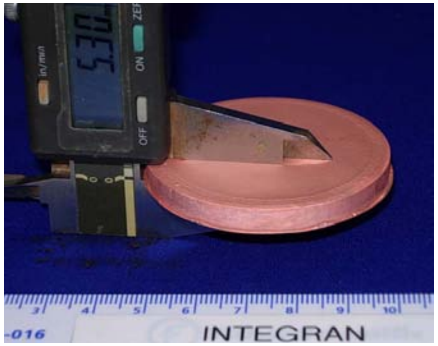
Phase I consisted of two main activities:

1) **Core technology development**
   - ♦ Nanostructured alloy development and fundamental material property characterization

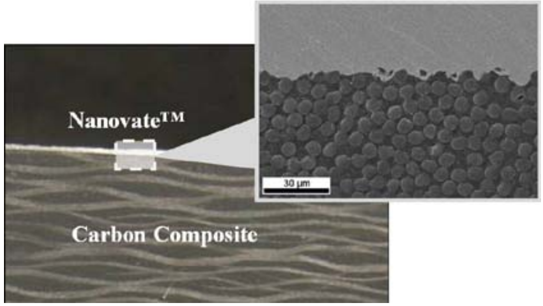
2) **Proof-of-concept demonstration** for three proposed application types
   - ♦ Bulk forms for bushings
   - ♦ Nanometal/composite hybrids for components typically formed from sheet metal
   - ♦ Nanometal hybrid wire

Phase II consisted:

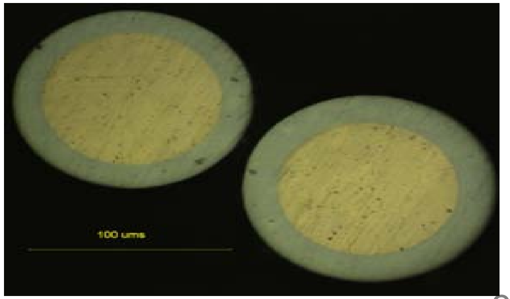
1) **Demonstration and Validation** of the three application types explored in Phase I



Nanostructured Copper – Bulk Form

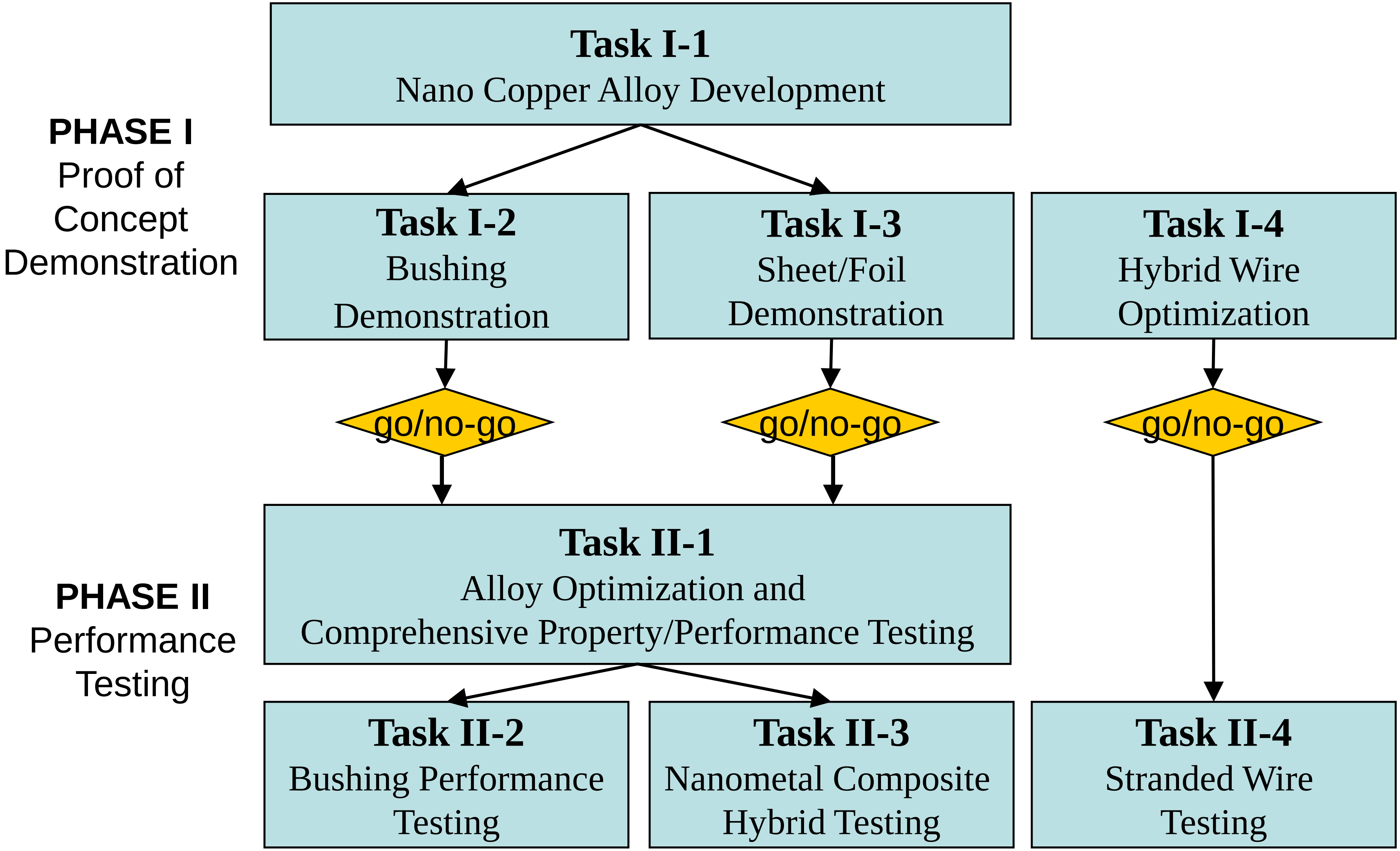


Nano/Composite Hybrid – Sheet Form



NanoConductor – Wire Form

Technical Approach



Summary of Phase I Alloy Development

System	Roughness (R_a, µm)	Microhardness (HV)	Taber Wear (mg/1000)	Friction (vs. 440C SS)	Ductility
C17200 TF00	--	393 ± 10	72 ± 5	0.8-1.0	Low
nCu (Pyro)	0.7-0.8	200 ± 10	76 ± 14	0.7-0.8	Medium
nCu (Sulfate)	0.8-1.0	200 ± 10	N/D	0.8-0.9	Medium
nCu + TF/D	0.5	223 ± 9 (low D) 245 ± 3 (high D)	34 ± 7 (low D) 9 ± 2 (high D)	0.3-0.4 (low D) 0.7-0.8 (high D)	Low
nCuSn	N/D	400-500	N/D	0.6-0.8	Very low
nCuNi	0.5-0.6	350-450	27 ± 7	0.7-0.9	Low/medium
nCo-alloy	0.4-0.5	440-500	18-19	0.3-0.5	Medium/high
nNiCo	0.8	477 ± 11	17 ± 2	0.7-1.0	Medium
nNiCo + GR	2.7	488 ± 38	N/D	0.3-0.4	Low
nNiCo + GR/D	2.1	504 ± 13	3 ± 2	0.9-1.1	Low

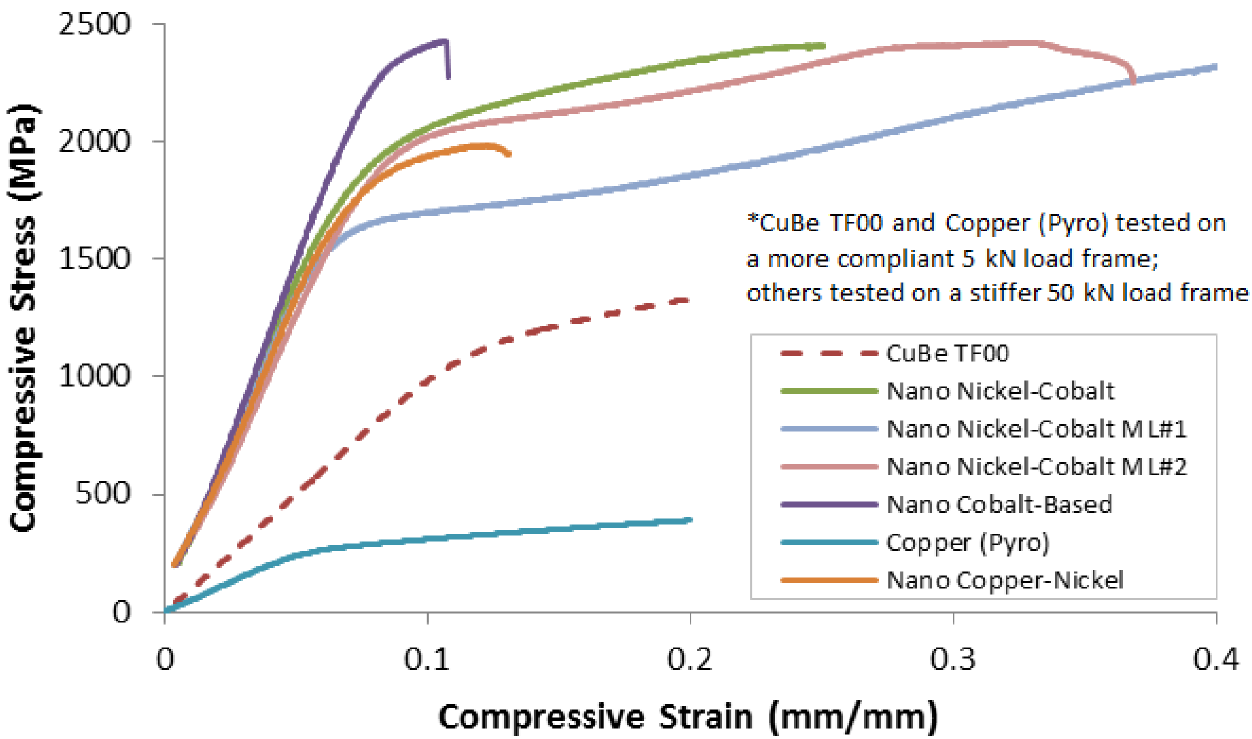
Nanometal Bushing Performance Testing

Background

- Cu-Be alloys still represent the best combination of strength, wear properties and cost for highly loaded bushing applications
- In Phase II, various electroformed nano alloys (Co, NiCo, CuNi and nCu) were tested and evaluated as an alternative to Cu-Be
- Performance testing included:
  - ♦ Tensile and compressive strength
  - ♦ Coefficient of friction against various ‘pin” materials
  - ♦ Galling resistance
  - ♦ High-load subscale bushing test

Mechanical Strength in Compression

- **Uniaxial Compression Testing (ASTM E9)**

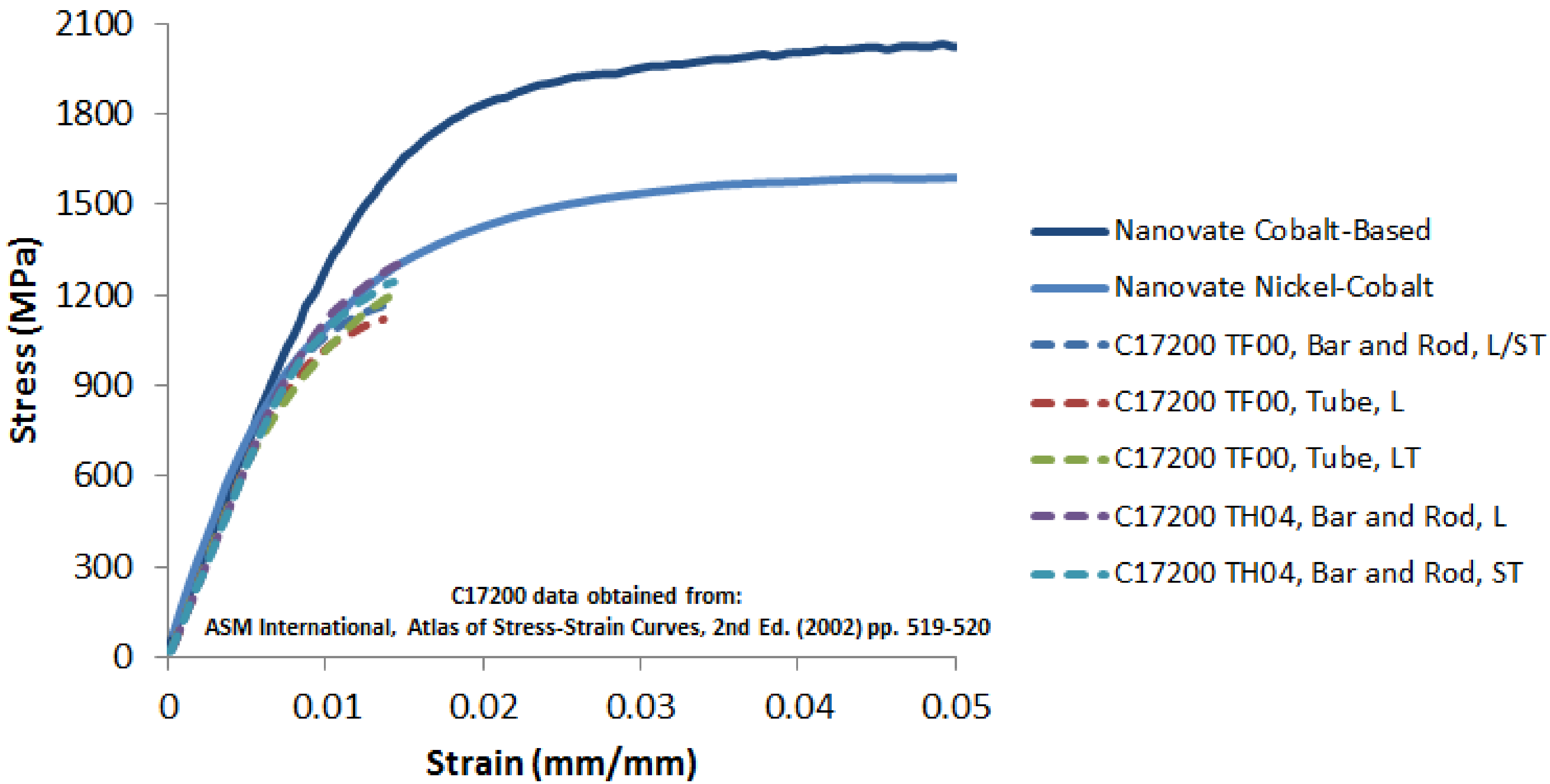


Material	0.2% Yield
CuBe TF00	973 ± 42 MPa
nNiCo	1508 ± 14 MPa
nNiCo ML1	1640 ± 40 MPa
nNiCo ML2	1373 ± 23 MPa
nCo-based	1967 ± 76 MPa
Cu (pyro)	<< CuBe TF00
nCuNi	1493 ± 61 MPa

All Nanometals investigated (except pure Cu) had signicantly higher compression strength than CuBe

Mechanical Strength in Tension

- **Uniaxial Tension Testing (ASTM E8)**



Tensile performance of Integran's Nanovate cobalt-based and nickel-cobalt metals is superior to copper beryllium (peak hardness);

Mechanical Property Summary

Nanostructured cobalt-based alloy has much higher compressive and tensile strength than conventional bushing materials

Material	Compression Strength ksi (MPa)	Tensile Yield Strength ksi (MPa)	Tensile Ultimate Strength ksi (MPa)	Tensile Modulus of Elasticity (GPa)
Nanostructured Cobalt Alloy	285 ksi (1967 MPa)	225 ksi (1550 MPa)	290 ksi (2000 MPa)	18855 ksi (130 GPa)
Copper Beryllium (C17200-TH04)	142 ksi (973 MPa)	172 ksi (1185 MPa)	190 ksi (1310 MPa)	18855 ksi (130 GPa)
Nickel Aluminum Bronze (C63000)	110 ksi (760 MPa)	68 ksi (470 MPa)	110 ksi (760 MPa)	16700 ksi (115 GPa)

Summary of Frictional Properties

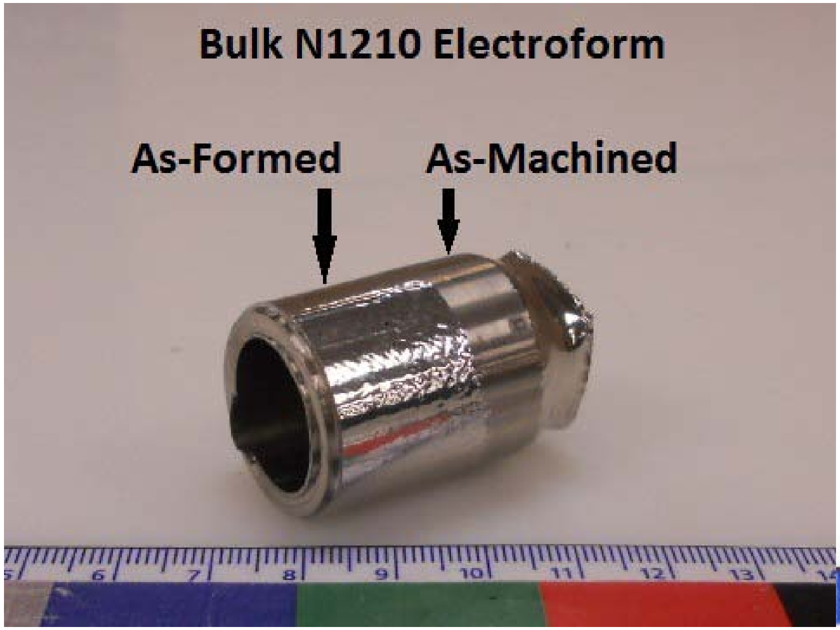
Nanostructured cobalt-based bushings have low coefficient of friction against standard mating pin materials

Bushing /Mating Material	Hard Chrome coated HSS	HVOF (CoCr-WC) coated HSS	Nano Cobalt coated HSS
Nanostructured Cobalt Alloy	0.42	0.46	0.36
Copper Beryllium (C17200-TH04)	0.73	N/A	0.65
Nickel Aluminum Bronze (C63000)	0.48	0.45	0.45

*COF obtained from Pin-on-disk testing per ASTM G99

Subscale Bushing Testing

Fabricated solid nanostructured bushings via electroforming for sub-scale busing testing

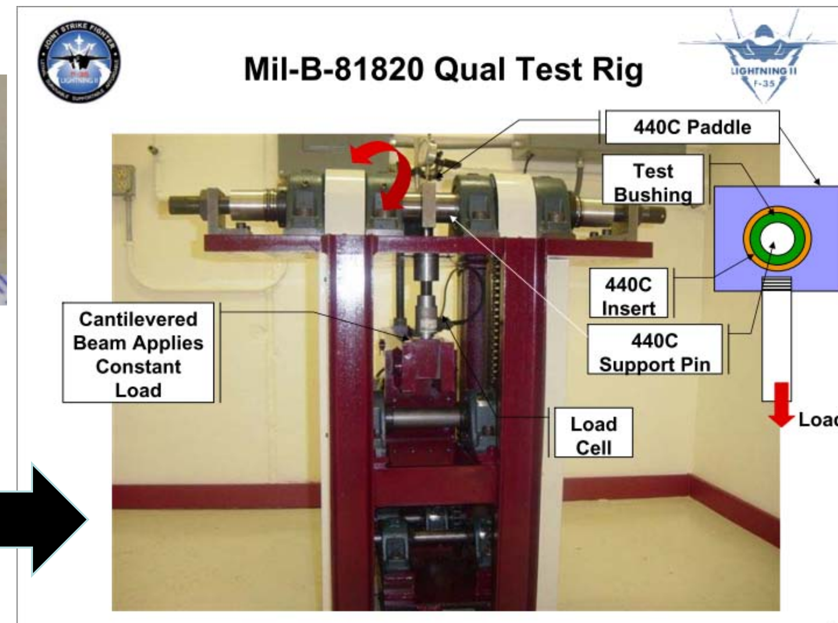


Geometry specific to
LHM-010 bushing test
(Tested at Cradin Aerospace)

Subscale Bushing Testing

- **Task II-2:** **Bushing Performance Testing**
  - ♦ **Bushings fabricated to LHM-010/MIL-B-81820 and tested by Cradin Aerospace (Boerne, TX) using a hardened 440C steel pin**
  - ♦ **Test consists of loading the pin in 200 lbs load increments and rotating ±45° for 200 cycles before stepping up to the next load**
  - ♦ **Pass consists of loading to 10,000 lbs (~50 ksi bearing stress) and run-out of 2000 cycles**

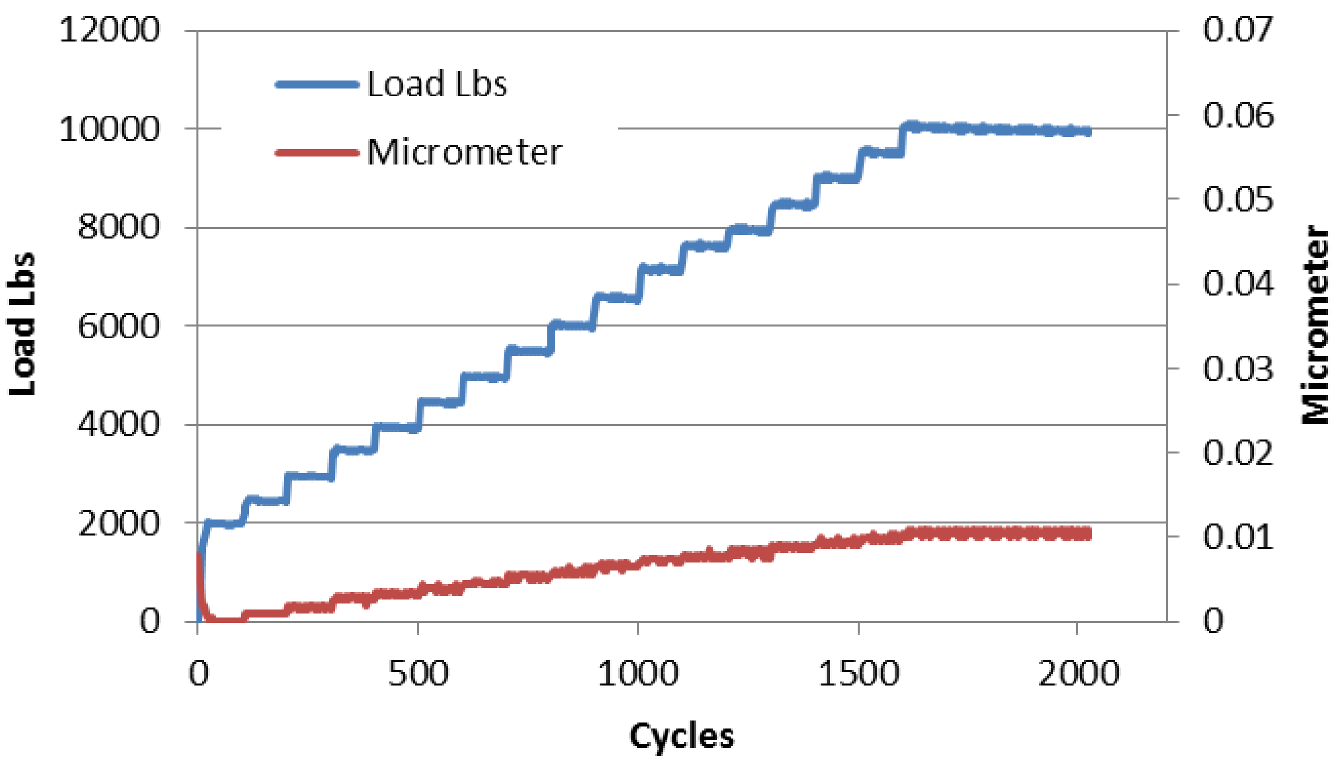
Image from Scott Fetter, 2009 ASETS Presentation
Cradin Aerospace Equipment



Sub-scale Bushing Performance

Nano Co-alloy bushings performed exceptionally well

- **Excellent alloy strength; Low bushing noise; Low bushing temperature increase (10,000lbs = ~50ksi bearing stress)**

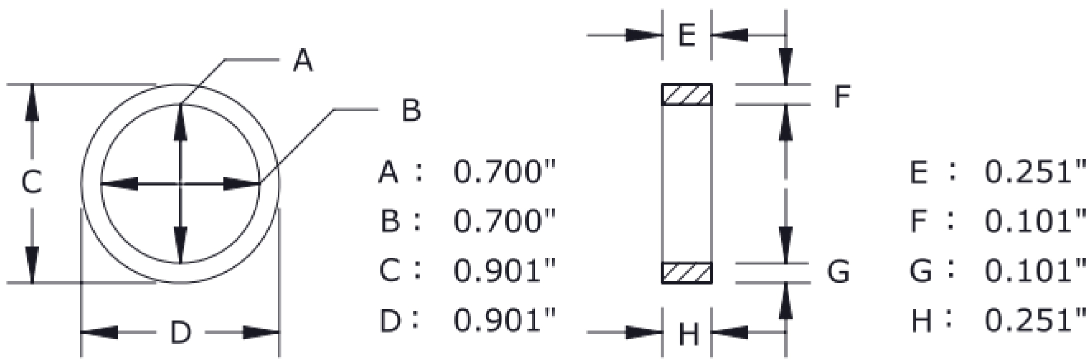


Subscale Bushing Performance

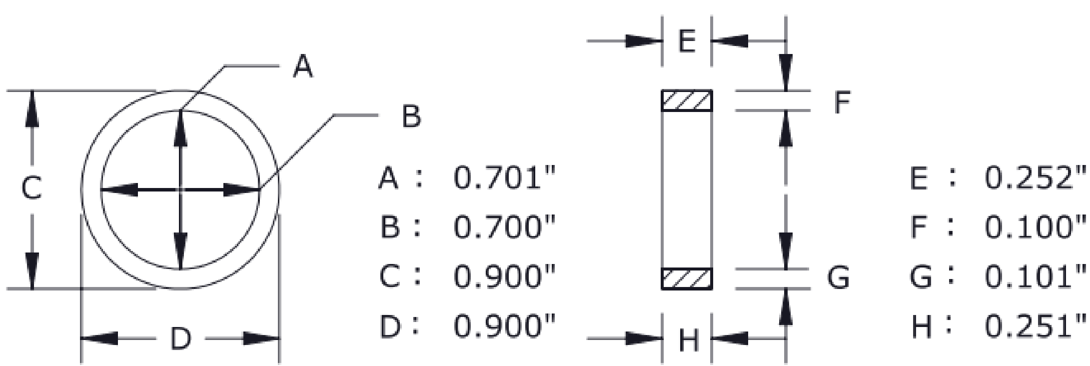
Nanovate bushings have minimal deformation

- Less than 0.001” wear and no measureable wall flattening

Dimensions - Prior to Testing



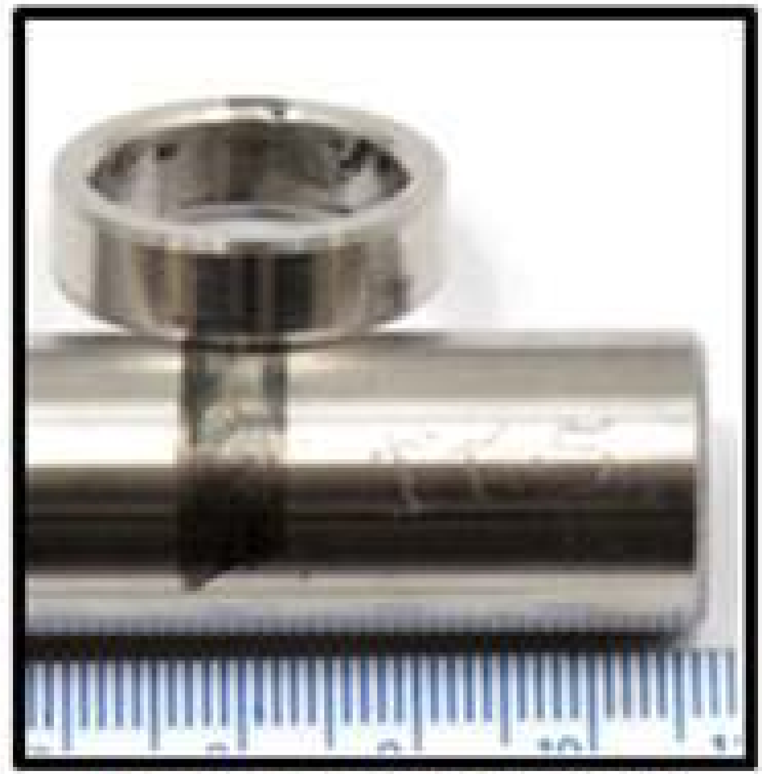
Dimensions - After Testing



Sub-scale Bushing Performance

Nanovate bushings perform favourably to CuBe:

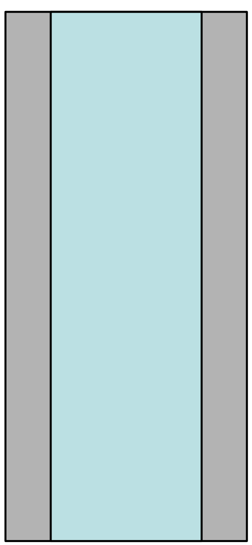
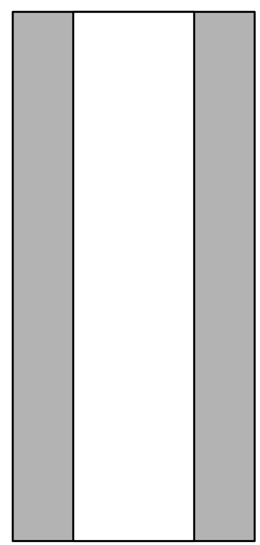
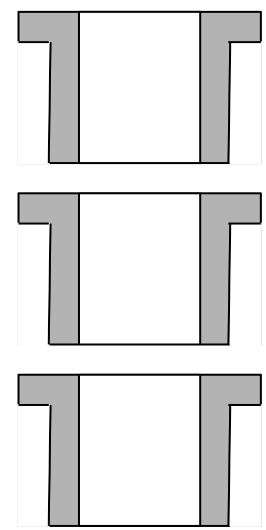
Cu-Be Bushing: MP 35N Pin
1725 cycles total
125 cycles at 10,000 lbs



Nano Co-alloy Bushing: 440C Pin
2000 cycles total
400 cycles at 10,000 lbs

Electroformed Nanometal Bushings

- Near Net Shape Manufacturing Process with high ‘buy-to-fly’ ratio
- Cost effective due to less material waste during machining

Step 1 - Electroform desired thickness (~0.25”) onto temporary mandrel	**Step 2 -** Remove mandrel	**Step 3 -** Machine Bushings
		

Prototype Nanometal Bushings

Nanovate bushings samples – Diameter range from 0.5” to 2.5” fabricated to date

Cost Analysis

ROM Cost Analysis

- Additive manufacturing approach **significantly reduces <u>material waste</u>** and **<u>cost</u>.**

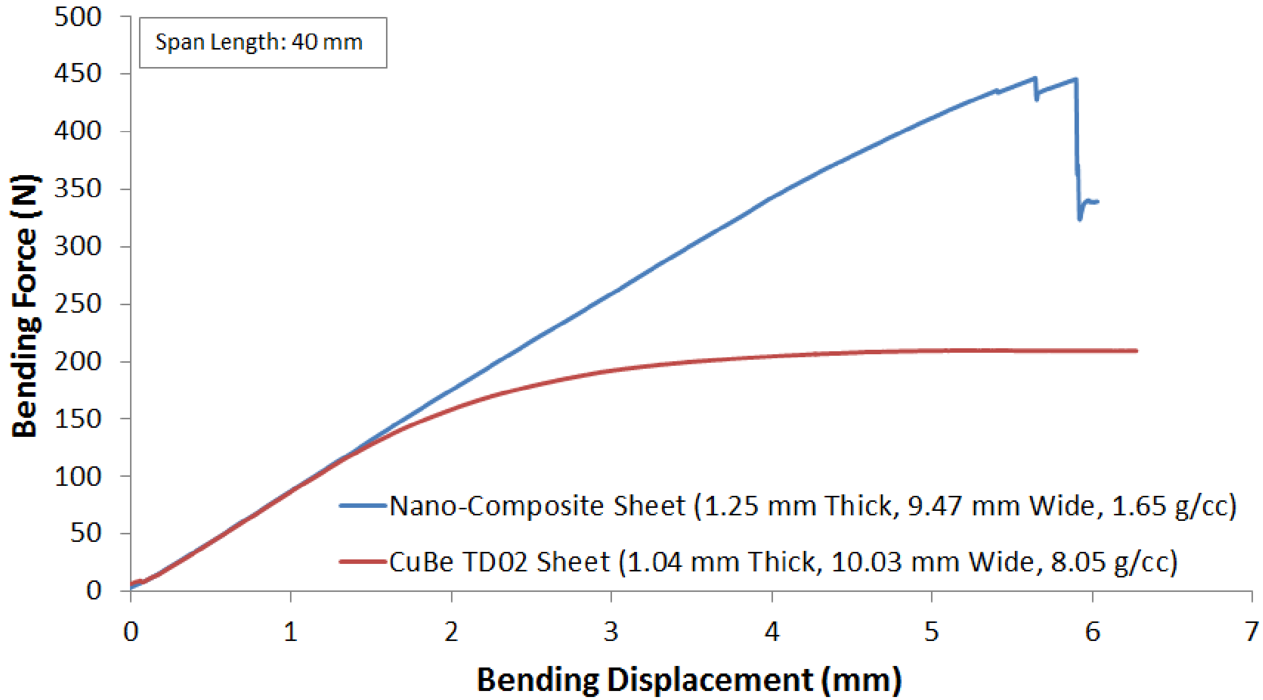
Material	Bushing Diameter	Material Required (lbs)	Material Cost ($)	Material Waste (lbs)
CuBe	2”	10.3	$124	86%
	3”	23.2	$279	90%
	4”	41.3	$496	93%
nCo-alloy (Additive Manufacturing)	2”	1.4	$52 to $173	-
	3”	2.3	$81 to $271	-
	4”	3.1	$111 to $369	-

- **Assumptions – CuBe bushing machined from solid rod to 0.25” wall thickness, 12” rod length, Cost of CuBe: 12$/lb, Cost of electroformed nCo: 3-10x base metal cost (36-120$/lb)**

Summary – Nanometal Hybrid Foil

Proof-of-Concept for Sheet/Foil Applications

- **Nanometal-composite hybrids can be designed to possess similar bending stiffness and higher elastic limit at similar sheet thickness but at <30% the weight of copper-beryllium with improved fatigue resistance**



Results Summary

- SERDP Project was successful in meeting original objectives
- Electroformed nano Co-alloy was tested and evaluated as an alternative to Cu-Be, demonstrating:
  - Significantly higher tensile and compressive yield strength than CuBe
  - Low coefficient of friction against various ‘pin” materials
  - Excellent galling resistance
  - Superior performance than CuBe in highly-loaded subscale bushing test
- Nanometal/Composite Hybrid show good promise for leaf spring/contact
- Looking for interested DoD and commercial partners to continue the project to the Dem/Val stage.