FINAL REPORT

NANOSTRUCTURED COPPER ALLOYS AS AN ALTERNATIVE TO COPPER-BERYLLIUM

SERDP Project WP-2137

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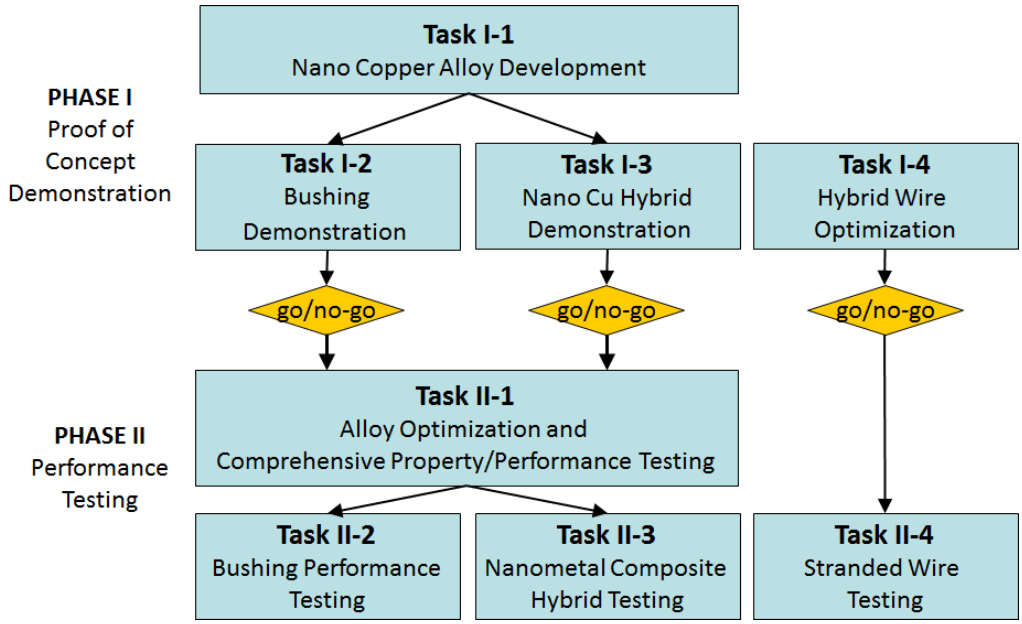
EXECUTIVE SUMMARY

SERDP Project WP-2137 "Nanostructured Copper Alloys as an Alternative to Copper-Beryllium" was recently completed by Integran Technologies, Inc. The main objective of the project was to develop and validate a cost-effective and environmentally-benign nanocrystalline electroplating/electroforming process that is capable of producing material, both for structural and functional components, that fully conforms to the mechanical and electrical property requirements for current and future copper-beryllium (CuBe) alloy needs and applications. The primary technical approach used in the project was to investigate Integran's proprietary nanotechnology processing methods to optimize the material properties via microstructural design and control; thereby employing grain refinement to the nano-scale (instead of age-hardening with CuBe or work-hardening with current CuBe alternatives) to produce suitable alternative materials to CuBe for insertion into applications within the defense sector. The technology is based upon Integran's nanostructured materials (e.g., high strength, high wear resistance, high fatigue performance, excellent corrosion resistance, low coefficient of friction, excellent coating adhesion, and low roughness) made by pulse electrodeposition, which allows for the retention of numerous benefits associated with plating (e.g., low cost, near-net-shape processing, low buy-to-fly ratio, and non-line-of-sight application).

The project consisted of two phases: Phase I – "Proof-of-concept demonstration" and Phase II – "Process optimization and performance testing" and focused on demonstrating the technology in three distinct product forms: i) bulk material for rod/bushing applications; ii) Nanometal/composite hybrids for components typically formed from sheet metal; and iii) Nanometal enabled conductor wire . A flow chart showing an overview of the tasks is included below.



In Phase I, the use of pulse plating with environmentally-benign plating solutions was found to produce nanostructured materials having a number of significant benefits as a CuBe alternative, including: 1) high strength, 2) good hardness, 3) high wear resistance, 4) low friction, and 5) good ductility. These materials

could be produced with low surface roughness, low stress, no porosity, and moderate-to-high build rates; attributes important for the near-net generation of bulk forms. Of importance for the fabrication of Nanometal/composite hybrid parts and stand-alone textured films, these materials could also be plated in thin electroformed shapes and applied to composite substrates with high adhesion. For the fabrication of Nanometal-enabled conductors, these materials could be plated continuously on copper wire.

Phase II continued the work from Phase I to a demonstration and validation scale, effectively demonstrating that pulse plating with environmentally-benign metal/alloy plating solutions can produce nanostructured materials that have a number of significant benefits over CuBe, and that conform to the property requirements for current and future CuBe alloy needs within the DoD. The most promising nanostructured material systems for CuBe-replacement applications identified in Phase I were further optimized and tested in Phase II, including: nanostructured copper (nano Cu), nanostructured copper nickel (nano CuNi), nanostructured nickel-cobalt (nano NiCo) alloy and nanostructured cobalt (nano Co) alloy. The successful conclusion of Phase II demonstrated and validated the manufacturing process and performance of the nanostructured materials in the three distinct product forms: i) bushing applications; ii) Nanometal/composite hybrids for components typically formed from sheet metal; and iii) Nanometal enabled conductor wire. The main technical highlights for each of these three areas are summarized below.

Bushing Applications – Nanostructured cobalt alloy bushings, fabricated in near net shape with a very high buy-to-fly ratio, possessed superior mechanical properties and enhanced performance compared to CuBe (and even to emerging CuBe alternatives). The nano cobalt alloy bushings have significantly higher hardness, tensile and compressive strength and showed no wear, no galling, no permanent deformation, less noise, and better friction in the sub-scale bushing test when compared against CuBe.

Sheet/Foil Applications – Integran's nanostructured metal in sheet/foil were shown to possess a number of benefits over CuBe including excellent fatigue strength, electrical conductivity, and could be combined with carbon fiber composite to generate a high-quality hybrid with higher strength and stiffness at a significantly reduced weight.

High Strength Wire Applications – The Nanometal/copper hybrid wire manufacturing process was successfully scaled to produce over 20,000 feet of wire for further demonstration/validation testing. The wire was shown to generate high-strength conductor wire with similar mechanical properties as the incumbent CuBe wire with improved conductivity. A minor surface defect found on the wire however, prevented the ability to strand the wire and perform full scale validation testing.

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1.0 INTRODUCTION

1.1 COPPER-BERYLLIUM (CUBE)

Copper-beryllium (CuBe) alloys are used extensively by the Department of Defense (DoD) in applications typically requiring one or more of the following attributes: high mechanical strength and stiffness; moderate thermal and/or electrical conductivity; non-sparking; etc. Applications include bulk forms (e.g., rods and bushings), sheet (e.g., springs and electrical contacts), and wire (e.g., electrical wire). However, the Environmental Protection Agency (EPA) [1] lists beryllium (Be) as hazardous with inhalation of Be-containing particulate leading to inflammation of the lungs and chronic beryllium disease and lesion development in the lungs with long-term exposure. The EPA has also classified beryllium as a Group B1, probable human carcinogen; as such, the EPA strictly regulates the processing and handling of CuBe and its products. Various alternate material technologies have been developed, and the most promising concepts have, to some extent, found acceptance in various military and commercial CuBe-replacement roles. However, there is still a significant technology gap for replacing these CuBe parts on large manufacturing scales, particularly because of the manufacturing process required for some of these alternative materials.

One of the main reasons for the widespread use of CuBe alloys is their very high strength-to-density ratio, which can be achieved with relatively small alloying additions (generally less than 5% Be). Yield strength values in excess of 150 ksi (~1000 MPa), far greater than that of conventional pure copper, can easily be obtained by strengthening the CuBe alloys via age (or precipitation) hardening. However, beryllium is a toxic substance, and thus for both environmental and safety considerations, exposure levels must be minimized throughout the entire life cycle of the component (component manufacturing through its repair/rework, to scrap/recycle). Since copper is well-known to provide many of the basic physical properties required for aerospace bearings, bushings and contact materials (e.g., high thermal and electrical conductivity, excellent oxidation resistance, resistance to galling, resistance to sparking, non-magnetic, etc.), an ideal solution to the beryllium toxicity problem would be to strengthen Cu by an alternative means (such as nano-structuring), rather than introduce a wholesale alloy change.

The aerospace applications for CuBe alloys can be generally classified as being either electrical or mechanical. For electrical applications, the required properties of CuBe – typically used in the form of strip or wire – are high yield strength and mechanical resilience, as well as good electrical conductivity. Mechanical applications are predominantly bushings and bearings where the finished components are machined from bar or rod stock. As CuBe bearings and bushings are invariably lubricated in service, the desirable material properties of CuBe alloys are not generally required under normal hydrodynamic lubrication modes of operation, but rather become critical in the boundary and mixed film lubrication modes of operation where metal-metal contact can occur. Accordingly, the desirable mechanical properties for a CuBe alternative generally include: a low friction coefficient; good wear resistance; high yield strength; high fatigue strength; good resistance to galling; high conductivity; and other application-specific properties.

Nanostructured materials are known to provide increased yield strength, increased wear resistance, reduced friction coefficient, and improved fatigue strength, all relative to their coarse-grained conventional counterparts [2]. Elastic properties, corrosion resistance, as well as galling, thermal conductivity, sparking resistance and magnetic performance, are intrinsic to the base material (copper) and should not be affected by nano-processing [3]. Additional cost advantages are expected from eliminating the need for age hardening

treatments which are currently required with CuBe alloys.

1.2 EXISTING CUBE REPLACEMENT ALTERNATIVES

As a result of the increasing costs associated with regulation of Be-containing materials, there are significant ongoing efforts to develop effective CuBe-replacement technologies. The most promising materials (such as ACUBE 100, Toughmet®, Nitronic 60, BioDur CCM/ACUBE 100, aluminum bronze, as well as other alloys of Cu-Sn-Ni, Co-Cr-Mo, and stainless steel [4,5,6,]) have, to some extent, found acceptance in various military and commercial CuBe-replacement roles. Reported [4-6] properties of CuBe-replacement alloys (particular to the bushing application) are shown in Table 1.

Table 1: Summary of properties of current CuBe-replacement alloys for bushing applications.

Alloy	Yield strength (MPa)	Elongation (%)	Hardness (VHN)	Coefficient of Friction*	Wear Rate ($mm^3/N\cdot m$)*	Workability
CuBe	~1,000	3-8	354-390	~0.78-0.82	$\sim 3\times10^{-4}$	Good
Al-bronze (AMS 4640)	~400	--	--	~0.69	$18\text{-}19\times10^{-4}$	High
Cu-Sn-Ni (AMS 4596)	~830-900	--	--	~0.71	$\sim 5\times10^{-4}$	Good
Cu-15Ni-8Sn (ToughMet®)	~740	3-10	275-290	--	--	Excellent
Co-Cr-Mo (BioDur CCM)†	~590-830	26	275-290	--	--	Excellent
Nitronic 60 (AMS 5848)	~750-970	--	--	~0.44	$\sim 1\times10^{-4}$	--
HBN 304	~655	--	--	--	--	--
QuesTek Cuprium	~920	~3-8	--	--	--	Good

*Mating material is not disclosed, though brass mating material appears to be shown in reference [5].
†Carpenter has made a variant of this alloy under the name ACUBE 100 as a CuBe replacement.

In general, these replacement technologies possess subsets of the required mechanical, electrical, wear, and thermal properties possessed by CuBe, which has allowed for replacement within particular applications. Al-bronze AMS 4640 has been used in bushing applications for some time due to its high wear resistance and thus has been considered a replacement for CuBe; however, its strength is not as high as CuBe. More recently, other CuBe alternatives receiving considerable attention are the Nitronic 60 and Co-Cr-Mo alloys, primarily because they have been shown to possess good performance in the MIL-B-81820 bushing tests. As a result, according to Fetter [6], in 2005 the F-35 changed all airframe bushings with diameter smaller than 2.5" due to good performance of Nitronic 60CW alloy. In 2006, promising results with the BioDur CCM (Co-Cr-Mo) alloy led to its qualification as an aerospace alloy [6]. Carpenter has made a variant of this Co-28Cr-6Mo alloy available specifically as a CuBe replacement (primarily for bushings) under the name ACUBE 100 [7]. However, some alloy processing requires cold or hot working which limits the ability to be produced at large scales, i.e., bushings larger than 2.5". As well, these alloys are iron and cobalt based, respectively, which limits their electrical and thermal characteristics as well as other benefits related to the utility of copper as the base metal. For example, under Aerospace Materials Standard AMS 5918, the ACUBE 100 material, an emerging CuBe-replacement alloy for bushing applications, possesses peak yield strengths up to 1,117 MPa (and hardness of 50 HRC) following warm working and aging.

Different than the existing CuBe replacement technologies, the focus of the present project built upon previous proprietary developments in the cost-effective electroforming of bulk quantities of nanocrystalline metals and alloys. The objective of the project was, to develop, optimize, and validate a nanostructured copper alloy that

satisfies the mechanical property requirements of SAE AMS 4533 for 98%Cu-2%Be alloy (CuBe, UNS C17200) in the form of a) near net shaped bar and rod geometries for use as bushing materials, b) flat sheet stock for us as electrical spring contacts and high specific stiffness/strength components, and c) high strength wire for military applications. As outlined in more detail below, Integran has applied its expertise and intellectual property in the area of metallurgical nanotechnology, as well as its previous experience with materials technology development programs, to demonstrate a cost-effective, environmentally-benign, nanostructured alternative to toxic beryllium-containing copper alloys. Moreover, the present approach has also provided the opportunity to selectively apply the alloy to finished and semi-finished components of virtually any substrate material (injection molded polymers, carbon fiber reinforced plastics (CFRP), lightweight metals and alloys), thus enabling potential further reductions in component cost and weight.

1.3 SYNTHESIS, STRUCTURE AND PROPERTIES OF ELECTRODEPOSITED NANOSCALE MATERIALS

1.3.1 Integran's Nanostructured Metal Processes

Integran Technologies Inc. (hereafter referred to as Integran) produces nanoscale metallic coatings for various applications and has been actively investigating CuBe replacement by evaluating possible alternative materials which can be fabricated via electrochemical processing. Integran takes advantage of its existing infrastructure of electrodeposition and achieves nanostructured materials to meet many customer requests through altering bath chemistry and applied electrical parameters. By reducing electrodeposit grain size to the nanoscale, metallic deposits with superior mechanical properties are produced. These improved mechanical properties, such as hardness, corrosion resistance, tensile strength, and low coefficient of friction, would be valuable to match or exceed the properties possessed by high-performance CuBe alloys.

Electrodeposited nanostructures have advanced rapidly to commercial application as a result of: 1) an established industrial infrastructure (i.e., electroplating and electroforming industries), 2) a relatively low cost of application whereby nanomaterials can be produced by simple modification of bath chemistries and electrical parameters used in current plating and electroforming operations, and 3) the capability in a single-step process to produce metals, alloys, and metal-matrix composites in various forms (i.e., coatings, free-standing complex shapes). The earliest systematic studies on the use of electrodeposition to produce nanocrystalline materials (i.e., materials with grain size values below 100 nm) were published in the late 1980's by the present applicants and the general conditions for producing nanocrystalline metals and alloys by electrodeposition are documented in US Patent No. 5,352,266 Oct. 4, 1994 and US Patent No. 5,433,797 July 18, 1995. SERDP has been instrumental in the advancement of electrodeposited nanostructures through its previous support of Integran in the development of a nanoscale Co-based hard chrome replacement technology (SERDP PP-1152), which has successfully advanced to the Dem/Val stage with a demonstration tank installation at NADEP-JAX (ESTCP PP-0411).

1.3.2 Environmental Impact of Integran's Nanostructured Metal Processes

With regard to potential environmental impact of Integran's nanostructured metal processes, it is anticipated that waste stream volumes and health hazards will be, for all intents and purposes, identical to those currently experienced with standard decorative nickel plating processes on a per tonne metal plated basis.

Regarding the environmental impact of the base metals generated during these processes, Integran's nanostructured materials generally achieve their strength via grain size reduction to the nanoscale. This is to say that the materials are generally without added strengthening particulate e.g., tungsten carbide. Studies exist

e.g., [8,9] which suggest tungsten-containing cobalt and/or nickel hard metals (and in some cases, their precursors i.e., metal sulfate salts) are *reasonably anticipated to be human carcinogens*. Until a conclusion is reached, the EPA is continuing work to evaluate the environmental and health impacts of the base metals.

1.3.3 Integran's Nanostructured Copper Electroforming Process

Integran Technologies has recently developed the capability to produce nano-Cu with controlled average grain sizes ranging from >1 μm to as low as 40 nm with corresponding Vickers microhardness ranging from 50 VHN to 210 VHN. Integran has developed the ability to create ultrafine-grained copper with extremely low concentrations of deleterious impurities such as S, C, and O. The implication is that flexibility exists with respect to target microstructure and composition, depending on the product properties desired.

A previous development project investigated the use of nanostructured copper in shape charge liners. As part of this development, near net-shape 81 mm liners were electroformed out of nanostructured copper. High strain rate mechanical testing (Kolsky bar testing) revealed that the material had excellent mechanical properties at high strain rate with a yield strength >1,000 MPa. However, no conventional mechanical testing or wear testing was performed as part of this project.

Integran also has demonstrated electrochemical technology which can generate nanostructured copper sputter targets that are of commercial scale (scale-up from 5 cm to 35.5 cm diameter at 6.4 mm thickness). These targets can be optimized in terms of grain size, and in important microstructural and chemical features of the material using Integran's "Nano + Grain Boundary Engineering (GBE)" processing technique (Canadian Patent No. 2,674,403).

1.4 NANOSTRUCTURED AND NANO-TWINNED COPPER LITERATURE

At the outset of Phase I, the project described herein proposed the following: instead of employing age hardening with beryllium-bearing copper alloys, the mechanical properties of alloys can be improved by grain size reduction/refinement to the nanostructured regime. While the use of Hall-Petch strengthening through grain refinement is well-known for many metals and alloys, the proposed approach explores the grain size range down into the nanocrystalline regime (less than 100 nm) – a region that is relatively unexplored for a number of metals, including copper. The effect grain size has on the yield strength and electrical resistivity is well known and Integran has the knowledge to demonstrate that high strength materials with good electrical (and thermal) conductivity can be obtained, which is of importance for electrical contact applications.

Regarding copper, it was estimated that its average grain size must be below 50 nm or so for the yield strength to achieve values commensurate with age-hardened CuBe (approximately 965 MPa). This has been difficult to achieve in the past, largely because most nano-Cu efforts have been based on synthesis techniques that involve nano-powder processing and subsequent compaction. While a nanocrystalline structure can indeed be achieved by the above two-step nano-powder process, it invariably results in residual material porosity and an associated loss of stiffness and ductility. In addition, fabrication of "real" engineering components from Cu nano-powders is impractical because of the high cost of producing the starting nano-powder and the lack of cost-effective sintering methods for fully compacted structures that are relatively free of deleterious contaminants. Hence, a key second feature of this innovation is our processing method: electrodeposition.

Stress-strain curves for an electrodeposited 'nano-twinned' material fabricated by the research group of K. Lu

at the Shenyang National Laboratory for Materials Science in China [10] show that the material is extremely strong, with a yield strength exceeding 900 MPa. In addition, the material exhibited an excellent elongation-to-failure of 13.5%. This study also employed Integran's proprietary pulsed electrodeposition techniques to deposit ultrafine-grained copper. However, the material in this study was unique because the microstructure exhibited massive twin formation with twin lamellae being approximately 15 nm apart from each other. Therefore, the material was not nanocrystalline *per se* (the average grain size was ~400 nm), but nevertheless exhibited a sufficient volume fraction of 'nano-twins' to induce a drastic mechanical property improvement in the material. Integran has previously developed a nanocrystalline pure copper with an average grain size (non-twinned) of less than 100 nm (i.e., approx. 75 nm). This nanostructured metal has been produced at the beaker scale to thicknesses of approximately 30 microns; also, in support of future industrial scale-up potential, it was produced at a very high deposition rate (approximately 0.25 mm/h). Very limited testing of this material has been conducted; measurements to date are as follows:

- Nano-indentation measurements have shown its hardness to be approximately 150-170 kg/mm^2. With further refinement and optimization, yield strength in excess of the minimum requirements specified in SAE AMS 4530 (965 MPa) should be attainable.
- The thermal stability of the material has been evaluated and has been shown capable of withstanding thermal exposure for up to 30 minutes at 250°C with negligible grain growth; if required, further improvement in thermal stability may be achieved by micro-alloying (e.g., by small Sn or P additions).
- The corrosion performance of this nanomaterial has been evaluated by the potentiodynamic polarization method in 0.1 M NaCl solution and shown to be comparable to that of conventional wrought pure copper.

2.0 PROJECT OBJECTIVES

The principal objective for the project was to demonstrate and validate the feasibility of utilizing electroformed and electrodeposited nanostructured metals/alloys as alternatives to CuBe alloys for mechanical and electrical applications, as outlined below. Section 3.1 provides a recap and rationale of the general approaches for each of the three product platforms. Section 3.2 reviews the overall project objectives, including the milestones reached in Phase I and those executed against during Phase II. Finally, Section 3.3 presents a summary of the work conducted during Phase II (which is then described in more detail in Section 4).

2.1 MANUFACTURABILITY OF NANOSTRUCTURED METALS AND ALLOYS FOR CUBE APPLICATIONS

2.1.1 Bulk CuBe

Due to the well-established copper electrowinning industry, the manufacturability of bulk nano Cu alloys for a number of CuBe replacement applications is expected to be commercially viable. The copper electrowinning industry produces large amounts of high purity copper every year. For instance, in the U.S. alone, 550 tons of Cu is processed via electrowinning each year [11]. As the synthesis method used in this program uses the same equipment as that for Cu electrowinning, the manufacturing costs are expected to be similar. Electrowon copper meets the requirements of ASTM B115, Specification for Electrolytic Cathode Copper, which is traded on the world's metal exchanges**.** A typical electrowinning operation can produce about 80 kg of copper on one copper cathode sheet in 10 days. As multiple sheets can be produced at the same time, the volume of material produced can be quite large. As the nanostructured material will applied in a coating-type process, however, there will be practical limits to the wall thickness, which at this time is estimated to be approximately 0.6 cm to

1.3 cm thick. Due to this limitation, near net shape components will be manufactured. For example, for a 6.4 cm diameter bushing, the nano-Cu alloy will be deposited onto a temporary mandrel in the form of a rod (approximately 30-60 cm in length) with an OD close to 6.4 cm. After depositing approximately 0.6 cm, the nano-Cu alloy will be mechanically removed from the rod, leaving a tube with a 6.4 cm ID and 0.6 cm wall thickness. The tube can then be cut into multiple sections resulting in near-net shape bushings that only need minor post processing. This manufacturing method is expected to provide a very high buy-to-fly ratio, which is the mass of material required to machine a part compared to the mass of material in the finished part.

2.1.2 Next Generation Nanostructured Hybrids

CuBe is commonly used because of its high specific stiffness and strength combined with other properties such as electrical and thermal conductivity and high temperature performance. The opportunity exists to selectively apply the proposed nano-Cu alloy to finished and semi-finished components of virtually any substrate material (injection molded polymers, carbon reinforced fiber composites, lightweight metals and alloys) thus enabling potential reductions in component cost and weight. Integran has recently completed a number of projects involving combining nanostructured metals with high specific strength and stiffness carbon fiber reinforced plastic (CFRP) materials to achieve a hybrid material with properties superior to the individual components. Specifically, Integran has developed the technology to use a nanostructured nickel-iron (nano NiFe) alloy on the ID of CFRP tubes to enable a novel lightweight composite actuator or cryogenic storage tanks. In both cases, the Nanometal/composite hybrid possessed superior properties over the composite alone, including improved specific bend strength, superior impact resistance, better high and low temperature performance, and improved burst strength. The key to the successful marrying of the two technologies was in obtaining an excellent bond between the two materials which was proven in the two aforementioned projects. A thin (100 µm) nano-NiFe coating on a CFRP substrate shows a significant improvement in bend strength provided by the nanometal coating in a three-point bend test. In the proposed project, Integran will investigate combining the nano-Cu alloy with CFRP substrates to enable extremely high specific strength/stiffness components with excellent thermal and electrical conductivity and improved high temperature performance over the composite alone.

2.1.3 Nanometal-Enabled Conductors for CuBe Replacement

Aircraft electrical wiring significantly contributes to an aircraft's overall weight, accounting for upwards of 2,300 kg in some models. In many cases, the electrical signal (control/systems) wiring is primarily limited by strength requirements; thus, the minimum wire size is limited by the material properties (tensile strength) of the conductor. A new electrical wire product with an enhanced strength-to-weight ratio can be utilized to significantly reduce the overall weight of the electrical wiring.

Integran has recently developed and performed a proof-of-concept demonstration that an enhanced strength-to-weight conductor material can result by utilizing a high-strength nanocrystalline cobalt (nano-Co) alloy in conjunction with a high-conductivity copper core material. The new Nanometal-enabled conductor has significantly higher strength-to-weight relative to the incumbent CuBe alloy (CS95 or high-strength conductor), while maintaining comparable conductivity. By utilizing this design, a 19-strand 24-gauge CS95 conductor may be replaced with a smaller sized 19-strand 26-gauge Nanometal-enabled conductor in order to realize significant weight reductions of approximately 30%. Additionally, this can eliminate the use of the toxic beryllium used to achieve the high-strength CS95 alloy. As reel-to-reel wire plating line is an established system currently used in industry, the Nanometal-enabled wire is expected to be competitive with CuBe wire.

2.2 DESCRIPTION OF MAJOR ACTIVITIES AND MILESTONES

The overall objectives for this project were to:

- Develop and validate a cost-effective and robust nanostructured metal/alloy electroplating/electroforming process that is capable of producing material that conforms to property requirements for current and future CuBe alloy needs/applications; and
- Demonstrate the process with three distinct product forms – 1) bulk material for rod and bushing applications, 2) Nanometal/composite for high specific strength/stiffness components, and 3) Nanometal cobalt/copper enabled conductor wire.

The specific objectives of this project, as discussed in the following sections, were addressed in eight Tasks:

Phase I – Proof-of-Concept Demonstration

- Task I-1 Process Development of Optimal Nanoscale Copper Alloy Systems
- Task I-2 Proof-of-Concept Demonstration for Bushings
- Task I-3 Proof-of-Concept Demonstration for Nanometal/Composite Hybrids
- Task I-4 Optimization of Nano Hybrid Wire

Phase II – Process Optimization and Performance Testing

- Task II-1 Comprehensive Property and Performance Testing of Nanostructured Cu Alloy
- Task II-2 Bushing Performance Testing
- Task II-3 Nanometal Composite Hybrid Testing
- Task II-4 Nanometal-Enabled Stranded Wire Testing

This project developed an understanding of the effect that microstructure (grain size, crystal structure/phase and composition) has on the properties and performance of nanostructured copper, copper alloys, and other metals/alloys as a method to determine an optimal *nanostructurally*-designed CuBe-replacement material.

3.0 PROJECT SUMMARY

3.1 PHASE I SUMMARY

A brief summary description for each task performed in Phase I is given below.

Task I-1 – Process Development of Optimal Nanoscale Metals/Alloy Systems

- Devised and evaluated a number of nanostructured copper, nanostructured copper alloy, and nanostructured metal systems, and performed fundamental property testing/analysis
- Test methods were selected based on relative importance to product form performance, e.g., specific for bushings, sheet/foil, and wire
- Test methods were also selected based on acquisition of fundamental properties readily comparable to CuBe benchmark
- Systems were down-selected based on process stability, optimize-ability, nanostructure integrity, overall appearance, and performance relative to commercial CuBe alloy C17200 in both the half-hard (TD02) and age-hardened (TF00) conditions

Task I-2 – Proof-of-Concept Demonstration for Bushings

- Demonstrated that thick, bulk nanostructured metal electroforms could be generated using the down-selected systems
- Demonstrated that electroformed bulk shapes could undergo minor machining operations and be shaped to specifications for bushing test MIL-B-82810/LHM-010 for testing in Phase II (Cradin Aerospace)

Task I-3 – Proof-of-Concept Demonstration for Nanometal/Composite Hybrids

- Demonstrated fabrication of two distinct forms of CuBe 'sheet' alternatives: thin nanostructured metal electroplated on to thin high-performance composite; and freestanding Nanometal foils
- Demonstrated that in composite hybrid form, excellent adhesion was obtained leading to significant improvements in weight-specific bending performance over CuBe
- In a parallel investigation with a commercial customer, free-standing nanostructured foil has been shown to be a suitable alternative for CuBe foil for an application that requires high fatigue performance with low electrical resistance

Task I-4 – Nanometal-enabled stranded wire testing

- Demonstrated successful re-starting of Nanometal-enabled conductor wire plating line
- Performed consistency testing of properties along 500-foot lengths
- Engaged in long-term property testing with large-volume wire supplier and testers

As outlined above, in Phase I of this project, copper was a primary element of focus for improvement via grain size reduction to the nanocrystalline regime. While a number of benefits were observed, it was found that the consistency of the nano-twinning process was limited at increased thicknesses, particularly to build up a thickness of 0.1" (or greater) for generation of bushings. Using Integran's knowledge and experience, a grain-refined copper material could be generated at thicknesses large enough to manufacture bushings; however, peak hardness of ~200 HV was found to be a maximum. Similar conclusions have been reached by other research groups conducting work on alternative 'alloy engineering' pathways for high-strength copper and copper alloys as replacements for CuBe. For example, Fodran and Misra [12] simultaneously developed a copper alloy and a cobalt alloy, both as potential CuBe replacements. In that case, it was found that the copper alloy possessed shortfalls in hardness and strength which did not make it a suitable CuBe replacement.

Integran Technologies has experience with microstructural engineering of nickel, cobalt, copper, and iron metals and their alloys; as such, Phase I of this project also focused on a range of alloys to determine those which may also be suited for the end application(s). More specifically, Integran found that different nanostructured metals may prove to be suitable replacements to CuBe depending on the end application. The results from beaker-scale tests were used to evaluate which alloys would be carried forward into Phase II activities, summarized in Table 2.

Table 2: Summary of properties collected during Phase I for down-selection.

System	Microhardness (MHV)	Taber Wear Index (mg/1000 cycles)	Friction (vs. 440C Steel)	Ductility
C17200 TD02	234 ± 3	60 ± 8	0.8-1.0	Medium/High
C17200 TF00	393 ± 10	72 ± 5*	0.8-1.0	Low/Medium
Nano Cu (Pyro)	200 ± 10	76 ± 14	**0.7-0.8**	**Medium/High**
Nano Cu (Sulfate)	200 ± 10	N/D	0.8-0.9	**Medium**
Nano Cu + TF/D	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
Nano CuSn	400-500	N/D	0.6-0.8	Low
Nano CuNi	**300-400**	**27 ± 7**	0.7-0.9	**Medium**
Nano Co alloy	**440-550**	**18-19**	**0.3-0.5**	**Medium**
Nano NiCo	**477 ± 11**	**17 ± 2**	0.7-1.0	**Medium**
Nano NiCo+GR	488 ± 38	N/D	0.3-0.4	Low
Nano NiCo+GR/D	504 ± 13	3 ± 2	0.9-1.1	Low

The processes down-selected from Phase I and with the most promising mechanical properties were evaluated based on process stability and consistency, as well as production rate. The results are summarized in Table 3.

Table 3: Summary of process stability and consistency for the down-selected processes.

System	Bath Stability	Electrical Waveform Optimized	Plating Efficiency	Plating Rate
Nano Cu (Pyro)	**High**	Pulse plating	75-85%	40 µm/hour
Nano CuNi	Medium/High	Pulse plating	85-95%	25 µm/hour
Nano Co alloy	**High**	Pulse plating	90-100%	**125 µm/hour**
Nano NiCo	**High**	Pulse plating	90-100%	60 µm/hour

Following Phase I, four nanostructured material variants were down-selected in Phase I and carried through into Phase II: 1) nanostructured copper (nano Cu), pyrophosphate chemistry, 2) nanostructured copper-nickel (nano CuNi), 3) nanostructured nickel-cobalt (nano NiCo), and 4) nanostructured cobalt (nano Co) alloy. These alloys were subsequently evaluated in Phase II as part of the three key product platforms.

3.2 PHASE II TASK PLAN OUTLINE AND SUMMARY

The task plan below was followed for Phase II of this project. Detailed discussions of the tasks and results are presented in the following sections.

Task II-1 – Comprehensive Property and Performance Testing of Nanostructured Metals/Alloys

- Scaled up, demonstrated, and validated a number of nanostructured metal and alloy systems, and continued performing property testing/analysis against CuBe (C17200/AMS4534).
- A number of property tests were performed, selected based on relative importance to product form performance, e.g., most specific for bushings but also relatable to other product platforms. Tests ASTM E8 (tension), ASTM E9 (compression), ASTM G98 (galling), ASTM B99 (pin-on-disc), and

ASTM B193/F390 (electrical conductivity).

Task II-2 – Bushing Performance Testing

- Manufactured near-net shape nanostructured metal electroforms, which underwent minor machining operations and be shaped to specifications for bushing test MIL-B-82810/LHM-010 for bushing testing by Cradin Aerospace (Boerne, TX).
- Analyzed uniformity of bushing properties through the bushing wall.
- Performed testing of bushings and compared against CuBe and emerging CuBe alternatives.

Task II-3 – Nanometal-Composite Hybrid Testing

- Scaled up the manufacturing of Nanometal-composite hybrids using off-the-shelf composite.
- Manufactured test samples for mechanical performance evaluation against CuBe, including ASTM D790 (three-point bending), ASTM D7136 (impact), and ASTM B593 (flexural fatigue).
- Scaled up the manufacturing of Nanometal foils/electroforms for application to other product groups, including replacements of hydroformed CuBe bellows. Worked with an industry partner to evaluate bellows manufactured from nanostructured metals.

Task II-4 – Nanometal-Enabled Stranded Wire Testing

- Scaled up wire processing to small commercial scales, i.e., 28,500+ feet in 1,500+ foot-lengths/spools.
- Supplied wire to commercial partner for evaluation as compared to commercial CuBe wire products.
- Commercial partner evaluated wire for single-strand performance (strength and conductivity) as well as strand-ability and integration into commercial products.

4.0 TASK II-1 – COMPREHENSIVE PROPERTY AND PERFORMANCE TESTING OF NANOSTRUCTURED METAL ALLOYS

4.1 TASK OBJECTIVES

The four nanostructured materials down-selected from Phase I were: nano Cu, nano CuNi, nano NiCo, and nano Co alloy. From these four materials, electrodeposited test samples (coupons) were produced and tested in accordance with standard methods. Testing included: compression testing (ASTM E9) and tension testing (ASTM E8) to evaluate strength and ductility; hardness (ASTM B578) to evaluate microhardness and its through-thickness consistency in bulk; pin-on-disc (ASTM G99) to evaluate sliding wear resistance; galling (ASTM G98) to evaluate adhesive wear resistance; and resistivity (ASTM B193/ASTM F390) to evaluate electrical conductivity. In all cases, materials were tested against CuBe alloys (C17200 and AMS4534). The following sections present the test results.

4.2 COMPRESSION TESTING (ASTM E9) AND TENSION TESTING (ASTM E8)

As part of the initial project, Integran proposed to investigate the tensile properties of the nanostructured metal alloys against standard CuBe. However, upon completion of Phase I, it was recommended by the SERDP committee to focus on the compression properties of the nanostructured metal alloys (particularly compressive yield strength) against standard CuBe. This is because of the importance of compression properties in the

bushing application. This data was then supplemented in this project with the tensile properties.

The compressive yield strengths of the down-selected nanostructured materials were measured following a modified procedure based on ASTM E9 using sub-sized samples that have been effectively used in previous studies of nanostructured materials [13,14]. Targeted sample dimensions will be approximately 2.2 × 2.2 × 3.5 mm^3 or having a similar slenderness ratio. The samples were manufactured via electro-discharge machining (EDM) from the thick nanostructured material fabricated in Task II-2 for bushing testing (Figure 1).

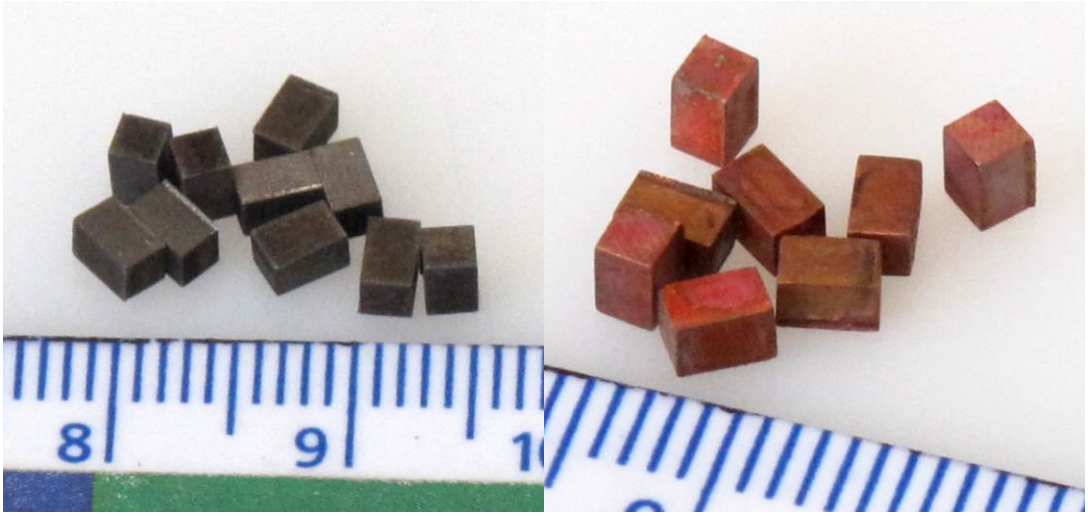


Figure 1: Nano NiCo (left) and nano Cu (right) sub-scale compression test samples fabricated via EDM.

Example compressive stress-strain curves for the down-selected nanostructured metal/alloy systems are shown in Figure 2. A summary of the compressive yield strengths (measured via the 0.2%-offset method) is provided in Table 4. For reference, also included is the average microhardness for the down-selected materials, taken as 20 points through the thickness of electroformed bushings (Task II-2). CuBe C17200 was used as the benchmark in the TF00 (peak age-hardened) condition; AMS 4534 (Revision B) was represented by the TH04 (solution heat treated, cold worked, and precipitation heat treated) condition. In Figure 2, both the TF00 and nano Cu samples were tested on a relatively compliant 5 kN load frame. The recorded elastic modulus was less than that expected due to the flexing of the test equipment. Moving up to a stiffer 50 kN load frame improved the readings, but the modulus was still lower than expected, presumably still due to machine compliance and lack of an extensometer or strain gage for these small samples. However, while modulus is low, it was expected that the 0.2%-offset yield strength did not change significantly with the compliance of the machine. In particular, the measured yield strength of CuBe TF00 (973 ± 42 MPa) was within the range for standard C17200 TF00 (140 ksi or 965 MPa [15]), which was slightly under the value stated for AMS4534B (TH04) CuBe (157 ksi or 1,082 MPa). Compared to CuBe, all nanostructured materials (except the nano Cu) possessed yield strength higher than CuBe (TF00 or TH04).

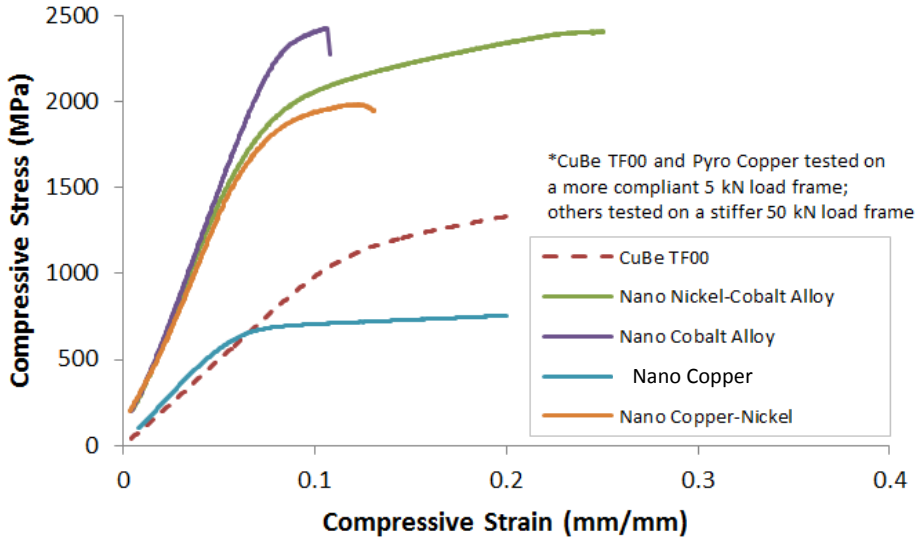


Figure 2: Summary of stress-strain curves in compression.

Table 4: Summary of compressive yield strength and microhardness of thick (0.100") electroforms.

Material	Yield Strength (MPa)	Microhardness (HV)
CuBe TF00	973 ± 42	394 ± 17
Nano Cu	505 ± 26	209 ± 11
Nano Co alloy	1,967 ± 76	546 ± 10†
Nano CuNi	1,493 ± 61	468 ± 19
Nano NiCo	1,508 ± 14	537 ± 11

†Variants of this material were also manufactured with lower hardness, e.g., down to 462 ± 11 HV.
Yield strength values are averages of three samples tested.

Tensile data for a number of the nanostructured materials was also collected to compare against CuBe in TF00 and TH04 conditions. Similar to the case for compression, Integran's nano Co alloy possessed significantly increased tensile yield strength (~1,600 MPa) over C17200 TF00 (~1,050 MPa) and TH04 (~1,150 MPa), shown in Figure 3 (data for C17200 TF00 and TH04 were obtained from the ASM Handbook published data [16]). Integran's nano Co alloy also had similar elastic modulus (~130 GPa) as CuBe. Integran's nano NiCo alloy possessed tensile yield strength (~1,000 MPa) similar to the CuBe alloys. Commensurate with the decreases in hardness, the tensile strengths of the nano Cu and nano CuNi alloys were less than the CuBe alloys. This comparison provides useful for the down-selection of suitable nanostructured metal systems, particularly for the bushing application.

To summarize, mechanical property and comparative testing of the down-selected nanostructured materials showed that Integran's nano Co alloy is superior to CuBe in both tension and compression. For the nano Co alloy, the yield strengths in both tension and compression are higher, and the hardness is consistent and higher through a bulk thickness. It is believed this will play a significant role in subsequent tasks.

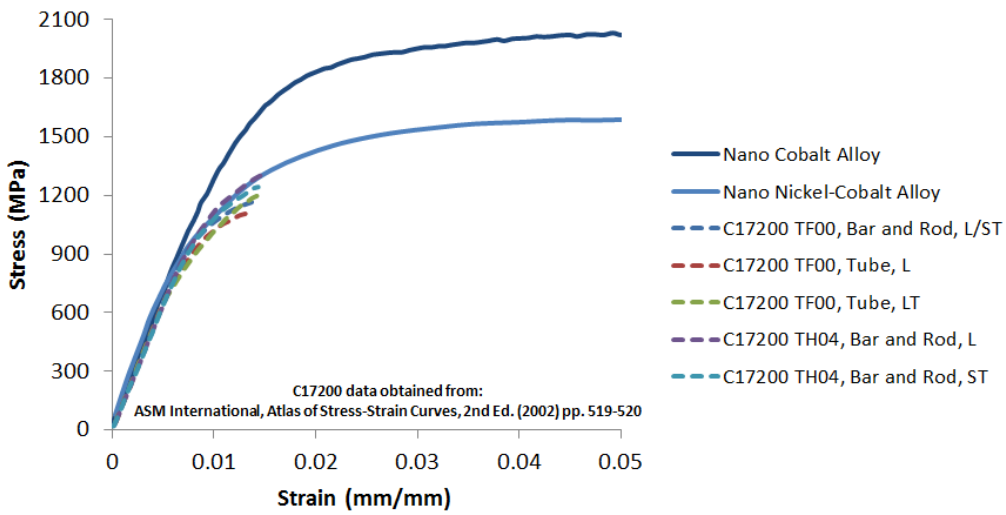


Figure 3: Tensile curves of CuBe TF00 and TH04 versus Integran's nanostructured metal alloys.

4.3 PIN-ON-DISC SLIDING WEAR TESTING

To evaluate Integran's nanostructured materials against incumbent materials for the bushing application, pin-on-disc (sliding wear) testing was performed after ASTM G99. Testing protocol was intended to be more complete and longer in duration than that performed during Phase I. The four down-selected nanostructured materials were included in the test as the "disc". CuBe and CuBe-alternative material nickel-aluminum bronze (C630) were also included for reference. The "pin" material was selected to be 440C stainless steel because it was the same material used for the "pin" in the sub-scale bushing tests (Task II-2). In cases where lubrication was also tested, Castrol Braycote® 3214 was selected as it is a multi-purpose, high-temperature, fully-synthetic aircraft grease, which is approved and qualified to MIL-PRF-32014; this product is intended for use in a variety of aircraft applications including landing gear assemblies and bearings, etc. In all cases, the sliding length was 1,000 m and force was 2 N.

Table 5: ASTM G99 pin-on-disc test summary data.

Disc (Integran Sample ID)	Pin	Friction Coefficient		Disc Wear Rate ($mm^3/N/m$)	
		Unlubricated	Lubricated	Unlubricated	Lubricated
CuBe	440C	0.76 ± 0.09	0.08 ± 0.02	3.21×10^{-5}	2.63×10^{-7}
Nano Co alloy (ZH926)	440C	**0.42 ± 0.09**	0.12 ± 0.02	**1.62×10^{-5}**	6.43×10^{-7}
Nano CuNi (J0013)	440C	0.75 ± 0.04	0.08 ± 0.03	3.98×10^{-5}	4.57×10^{-7}
Nano NiCo (STA40)	440C	0.81 ± 0.04	0.15 ± 0.05	8.31×10^{-5}	9.64×10^{-6}
Nano Cu (EF006)	440C	0.83 ± 0.07	0.04 ± 0.04	3.66×10^{-5}	1.30×10^{-6}
Aluminum Bronze	440C	0.32 ± 0.06		1.32×10^{-5}	

In general, it was found that the un-lubricated testing resulted in a pseudo steady-state friction coefficient for the duration of the test. For some materials including the CuBe and nano Co alloy (Figure 4), the data collected was considerably 'noisy', which was reflected in a relatively high standard deviation from the

average. This was not due to the loss of material during testing. In fact, shown in Table 5 CuBe and nano Co alloy (as well as Al-bronze) possessed the lowest disc wear rates. In addition to a low *disc* wear rate when un-lubricated, CuBe also possessed a low *pin* wear rate of 7.82×10^{-7} $mm^3/N/m$, bested only by nano Co alloy at 9.32×10^{-8} $mm^3/N/m$ (*an order of magnitude lower than CuBe!*). With the nano Cu sample, there was considerably less noise, presumed because of the decreased hardness of the material. For a number of coating materials, the wear rate was similar as that for CuBe. Only the nano NiCo alloy had a measurably higher wear rate against the 440C pin. Of the nanostructured materials, the nano Co alloy overall performed best in non-lubricated conditions.

In contrast, with the application of the lubricant, there was a more dynamic effect, i.e., a changing friction coefficient as a function of sliding wear length. This is believed to be due to a 'working-in' or dispersion of the lubricant. The entire data capture for CuBe, nano Co alloy, and nano Cu are summarized in Figure 4.

To summarize, pin-on-disc testing of the down-selected nanostructured materials showed that Integran's nano Co alloy is superior to CuBe when mated against 440C SS. For the nano Co alloy, the friction coefficient is significantly lower, the overall wear rate is lower, and there are no apparent negative effects of lubrication. It is believed this will play a significant role in the bushing testing, Task II-2.

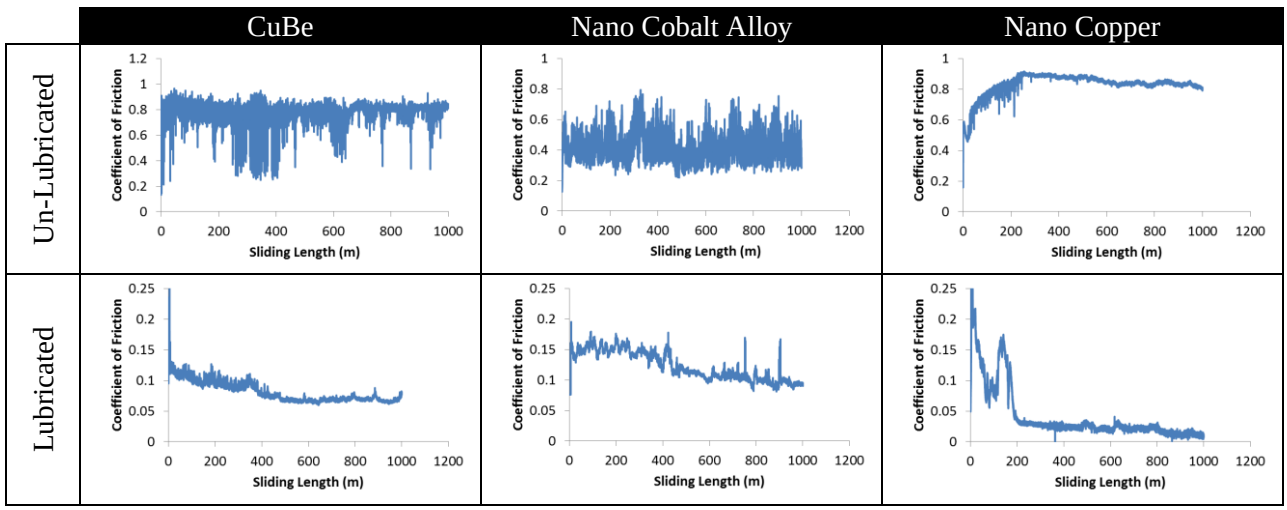
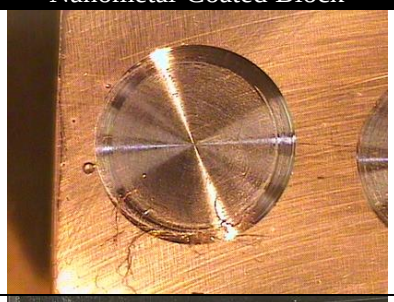
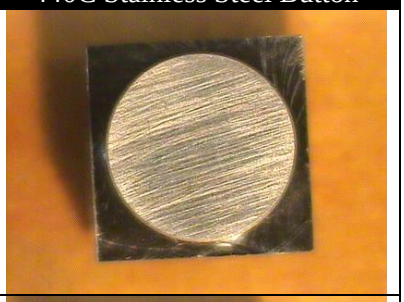
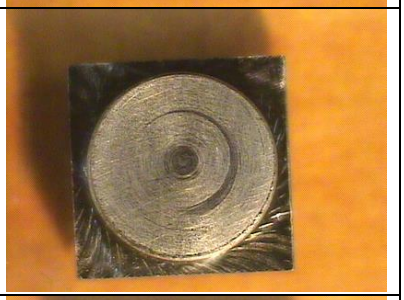
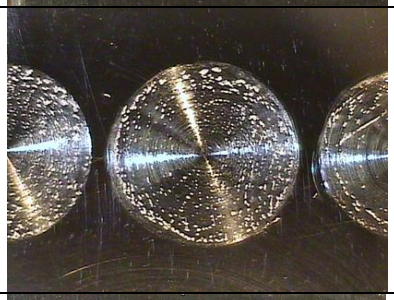
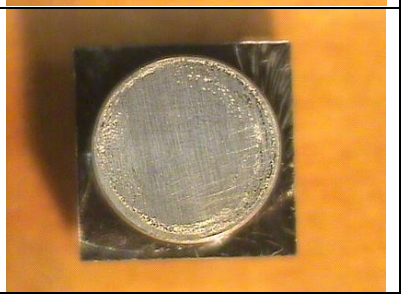


Figure 4: Pin-on-disc test results for nano Co alloy and nano Cu vs. CuBe.

4.4 GALLING TESTING

While not part of the initial proposal, upon completion of Phase I it was decided by the SERDP committee and Integran to include an evaluation of the galling resistance of the nanostructured metal alloys against standard CuBe. This is because of the importance of galling resistance (ASTM G98) in the bushing application. Bud Labs (Rochester, NY) was identified as a lab to perform this testing. Funding for these tests was taken from the mechanical testing budget in the program. To mirror the bushing test, Integran's coatings were compared in galling against hardened 440C steel buttons. The coating was applied as a ~100 micron-thick layer on hardened 4140/4142 steel flat, planed to a surface polish.

Table 6: Summary of ASTM G98 galling test results.

	Nanometal-Coated Block	440C Stainless Steel Button
Nano Cu (40 ksi)		
Nano Co alloy (40 ksi)		
Nano CuNi (10 ksi)		
Nano NiCo (10 ksi)		

The galling tests show that while Integran's nano Cu and nano Co materials possess good galling resistance (at least 40 ksi), nanostructured nickel-containing alloys experience galling under lower stresses. In comparison to CuBe, literature for Brush-Wellman Alloy 25 (a.k.a. C17200 with yield strength of 145 ksi/1,000 MPa) places the galling resistance against 440C stainless steel at over 50 ksi [17]. Furthermore, correlation between ASTM G98 galling resistance and bushing performance has been made with other high-performance CuBe alternatives for bushing applications, e.g., ACUBE 100 [7]. In specific, the ACUBE 100 material has a reported galling threshold stress of >20 ksi (>138 MPa) [Carpenter Technical Datasheet for ACUBE 100], while Integran's

nano Co alloy has demonstrated >40 ksi against 440C stainless steel.

4.5 RESISTIVITY TESTING

In order to evaluate the electrical conductivity of Integran's nanostructured materials compared to the incumbent CuBe, resistivity testing was performed after ASTM B193 using an in-line four-contact tester similar to that described in ASTM F390.

Table 7: Summary of room temperature conductivity of Integran's nanostructured materials versus CuBe.

Material	Resistivity (μΩ·cm)*	% IACS
100% IACS Copper	1.7	100%
CuBe C17200 TF00/TH04 [18]	6.2-7.8	22-28
Nano Cu	2.0	85.3
Nano CuNi	60.0	2.9
Nano NiCo	12.5	13.8
Nano Co Alloy	15.1	11.4

*Note: test current was 0.1487 A, sample length was 1.85 cm, and cross-sectional area ranged from 0.3-1.0 mm^2.

The resistivity measured in Integran's nano Cu material (2.0 μΩ·cm) is significantly less than that measured by Lu et al. [10] in their nanocrystalline (nc) copper foil at room temperature (~18 μΩ·cm). In addition, the resistivity measured in Integran's nano Cu material is *nearly as low as that achieved by Lu et al. in their nano-twinned copper foil* (1.75 ± 0.02 μΩ·cm). While Lu et al.'s nc-Cu had a smaller mean grain size (15 nm) than Integran's nano Cu, it is believed that the order of magnitude increase in resistivity in Lu et al.'s nc-Cu is due largely to significant impurities present in their deposit. In contrast, Integran's nano Cu plating process is based on an alkaline bath chemistry that generates materials with extremely high purity, which is commensurate with the data in Table 7.

Additional CuBe replacement alloys are available commercially for thin-foil/flat stock product forms. For example, JX Nippon Mining and Metals offers a NKT322 alloy, GIGALLOY®, which conforms to UNS alloy C19910. This alloy targets thin-foil switches, connectors, and the like. By inclusion of 2.9-3.4% Ti and 0.17-0.23% Fe, the material strength can be increased near that of CuBe (yield strength of 937 MPa, ultimate tensile strength of 1,013 MPa, and microhardness of 330 HV); however, the resultant conductivity drops to 10-13% IACS [19], i.e., similar to Integran's nano NiCo alloy and nano Co alloy.

At elevated temperatures, the resistivity of materials will change. For Integran's materials, specifically those considered as replacements to CuBe, it is critical that the nano-scale microstructure does not change significantly during heating to standard operating temperatures of the specific application, e.g., indicative of grain growth which would result in a loss of strength and hardness. Microstructural changes during heating can be observed in the form of inflections or changes in slope of resistivity as a function of temperature, e.g., [20]. Shown in Figure 5, there are no inflection points up to 250°C for down-selected nanostructured materials. The slope of resistivity as a function of temperature for each of the four down-selected materials is summarized in Table 8. Comparative slopes have been measured for other CuBe alloys, e.g., high-conductivity C17500, which has a temperature coefficient of approximately 0.0071 μΩ·cm/°C over a similar range [21].

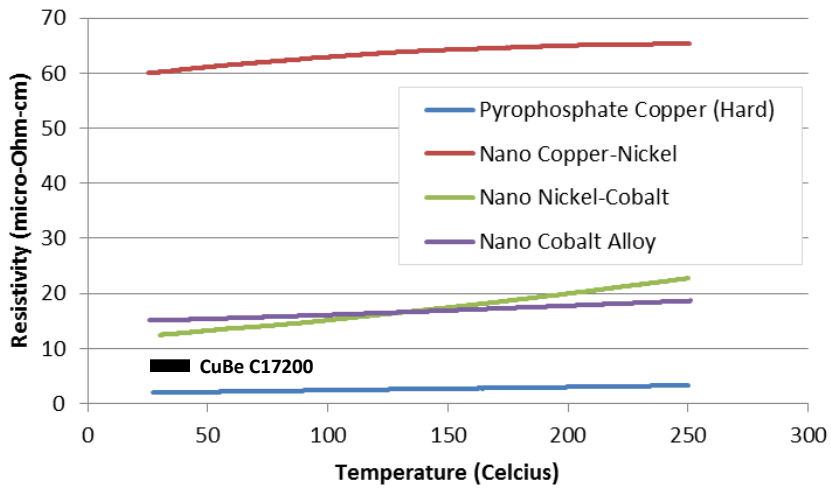


Figure 5: Electrical resistivity for the down-selected nanostructured metals/alloys as a function of temperature.

Table 8: Slope of electrical resistivity as a function of temperature (room temperature up to 100°C).

Material	ΔResistivity (μΩ·cm/°C), 25-100°C
Nano Cu	0.0058 (R^2 = 0.9962)
Nano CuNi	0.0401 (R^2 = 0.9966)
Nano NiCo	0.0385 (R^2 = 0.9962)
Nano Co Alloy	0.0134 (R^2 = 0.9974)
CuBe C17500	0.0071 [21]

5.0 TASK II-2 – BUSHING PERFORMANCE TESTING

5.1 TASK OBJECTIVES

The object of this task was to establish the performance of the down-selected nanostructured alloys against CuBe in a sub-scale, high-load bushing rig test. For this task Integran collaborated with Cradin Aerospace (Bourne, TX), an industry partner who has previously evaluated CuBe and CuBe alternative bushing materials against MIL-B-81820 – Navy Bushing Qualification (Note: MIL-B-81820 testing is now performed under Lockheed Martin procedure LHM-010). The pin OD (i.e., the surface applying the load to the bushing ID) is made of 440C steel hardened to 50 HRC minimum.

Figure 6 shows the mechanical drawing for the test bushings according to the LHM-010 (Lockheed Martin) test protocol. These bushings possess an ID of 0.700" and a wall thickness of 0.100" (2.54 mm) (mechanical drawing supplied by Cradin Aerospace). Also shown in Figure 6 is a picture of the MIL-B-81820/LHM-010 sub-scale bushing test rig (image from Reference [6]).

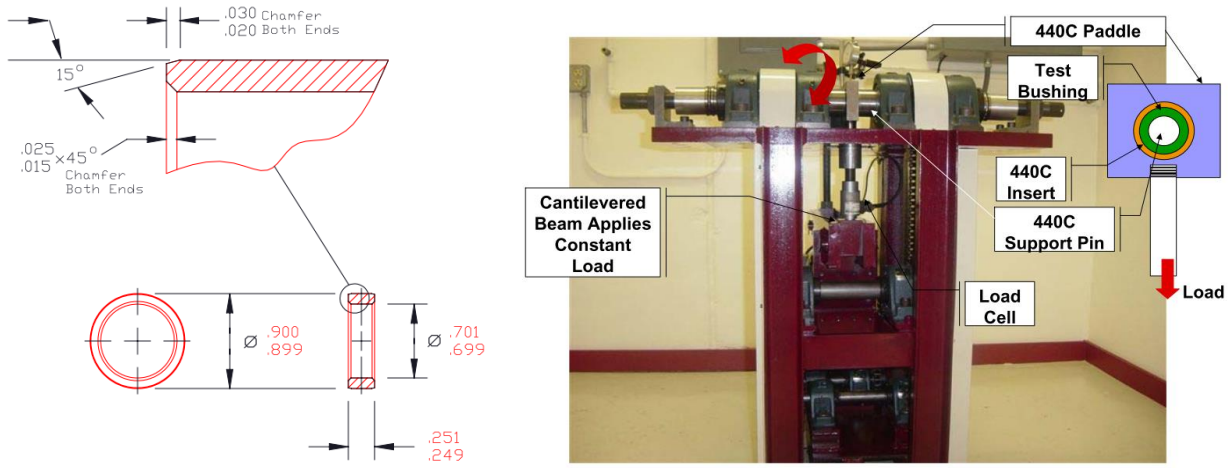


Figure 6: MIL-B-81820/LHM-010 sub-scale bushing test sample drawing (left) and test fixture (right).

The sub-scale bushing test involves applying a normal load to the bushing ID/pin OD interface and rotating through ±25° steady rotation while under load. The applied load starts at 2,000 lbs and increases 500 lbs every 100 cycles, to a maximum of 10,000 lbs (reached at 1,600 cycles). Run-out is considered at 2,000 cycles. Results for other CuBe and emerging CuBe-alternative materials in this test have been obtained in other studies, e.g., [6] (also performed by Cradin Aerospace).

Task II-2 of this program sought to manufacture and test a number of sub-scale bushings manufactured from the down-selected nanostructured metals/alloys. The nano Cu material system was not tested due to its insufficient hardness. In parallel, bushings were tested iteratively and bushing cross-sections were analyzed via microhardness.

5.2 MICROHARDNESS TESTING

In order to determine the uniformity of deposit properties over the course of the electroformed metal thickness (0.100" bushing wall), the microhardness profile as a function of bushing thickness was mapped for the down-selected metals/alloys. An example of hardness profile as a function of thickness in a machined Nanometal bushing (in this case, a nano-NiCo variant) is shown in Figure 7. In this profile, the majority of indents were made at the ID and the OD of the machined bushing. In general, there was no significant change in the hardness over the thickness of 2.54 mm: for example, the percent variation in hardness (standard deviation divided by the average, 20 measurements) from bushing cross-sections analyzed were found to be under 10% for all of the down-selected Nanometal platforms. Average microhardness (20 points) through the entire thickness (0.100") of the electroformed and machined bushing was presented earlier in Table 4.

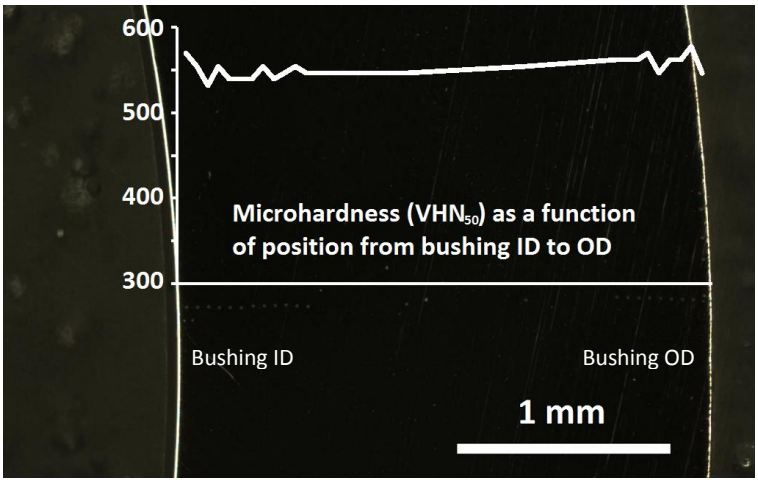


Figure 7: Example through-thickness microhardness profile in a machined Nanometal bushing.

5.3 MIL-B-81820/LHM-010 PERFORMANCE TESTING

During the entirety of this task, a number of bushings fabricated by Integran were tested in an iterative/optimizing manner. These bushings included those from the down-selected list but also included additional bushings with various engineered microstructures to further improve their performance. In general, it was found that bushings consisting of nano Co alloy had the best performance, significantly outperforming CuBe. In specific, shown in Figure 7, nano Co alloy bushings showed no signs of wear, galling, or permanent deformation on the ID or OD or thickness even after a bushing load of 10,000 lbs for 400 cycles. In contrast, CuBe bushings exhibited severe deformation, ID wear, and even spallation after a bushing load of 10,000 lbs for 125 cycles. In addition to the nano Co alloy with hardness 546 ± 10 HV (Table 4), additional variants of the nano Co alloy with reduced hardness (e.g., down to 462 ± 11 HV) were also tested. Despite the reduced hardness (even less than some nano NiCo alloy bushings), nano Co alloy bushings experienced the same *lack* of wear, galling, or permanent deformation even after 10,000 lbs as the harder nano Co alloy bushing.

The hardness of the nano copper thick electroform (209 ± 11 HV, Table 4) was considerably lower than that of CuBe. Based on the performance of a nickel-cobalt alloy bushing variant with similar hardness (Table 9), it was expected that this bushing would undergo excessive plastic deformation. The hardness of the nano CuNi electroform (468 ± 19 HV, Table 4) was more comparable to CuBe. However, due to the lower galling resistance of this alloy than even nano NiCo (Table 6), it was expected that this bushing would fail due to seizing to the pin.

The results of the tested bushings can be connected with the hardness (Table 4), sliding wear test performance (Table 5), and galling test performance (Table 6) of the down-selected nanostructured materials. Nickel and its alloys typically undergo undesirable galling when paired against stainless steels. On the other hand, cobalt and other HCP metals are typically galling resistant [22]. Following the bushing testing, the nano Co alloy (of the four down-selected materials) was most successful and did not show any failure after 2,000 cycles, despite some variants not having the highest hardness.

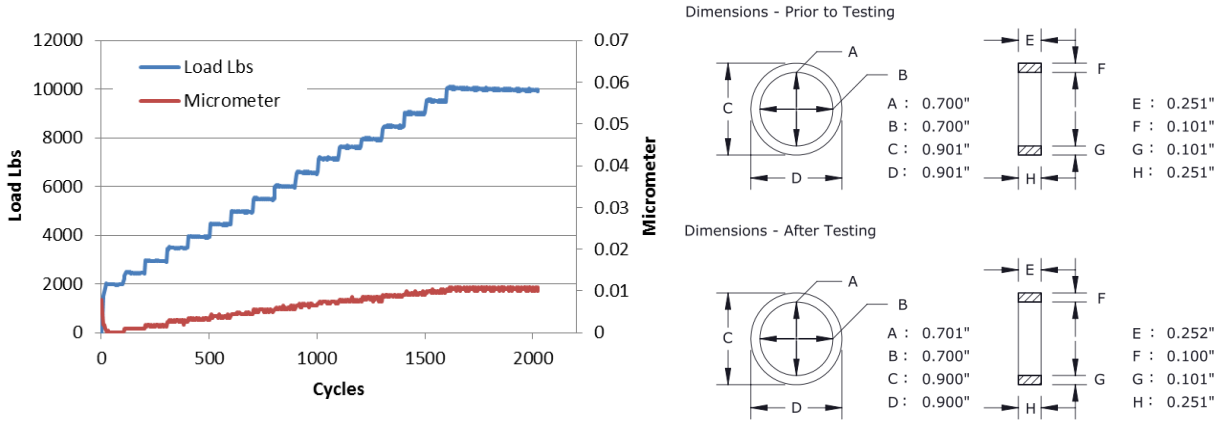


Figure 8: LHM-010 bushing test results (load versus deflection) for the nano Co alloy bushing.

CuBe bushing
MP 35N Pin
1,725 cycles total
125 cycles at 10,000 lbs

Nano Co Alloy bushing
440C Pin
2,000 cycles total
400 cycles at 10,000 lbs

Figure 9: Summary of bushing test results versus CuBe (CuBe results from [6]).

Fetter [6] has performed bushing testing for current and emerging CuBe replacement materials for bushings, i.e., ToughMet 3, Nitronic 60, and BioDur CCM (Figure 10). Of these, the BioDur CCM alloy (which is similar composition to the ACUBE 100 alloy) has extremely good performance as a bushing. Carpenter Technologies has also performed bushing testing of three materials including CuBe (AMS 4533), ACUBE 100 (warm worked), and AMS 5848 (a.k.a. Nitronic 60) [7]. While the CuBe alloy met the 10,000 lbs load, it experienced an average dimensional change of 0.016" in wall thickness and 0.054" in width. Worse, AMS 5848 did not reach the 10,000 lbs load but experienced an average dimensional change of 0.017" in wall thickness and 0.135" in width. The ACUBE 100 exceeded the 10,000 lbs load and experienced a negligible change in wall thickness and a width change of only 0.009". (Shown in Figure 8, Integran's nano Co alloy bushing(s) reached 10,000 lbs with negligible dimension changes.)

ToughMet 3TS bushing
MP 35N Pin
1,600 cycles total
Stopped at one cycle of 10,000 lbs

CW Nitronic 60 Bushing
MP 35N Pin
1,850 cycles total
250 cycles at 10,000 lbs

BioDur CCM Bushing
MP 35N Pin
Ran up to 12,000 lbs to 5,000 cycles with minimal (0.004”-0.005”) wear

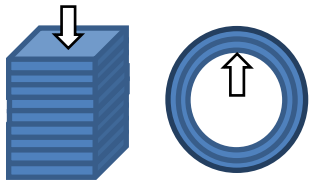
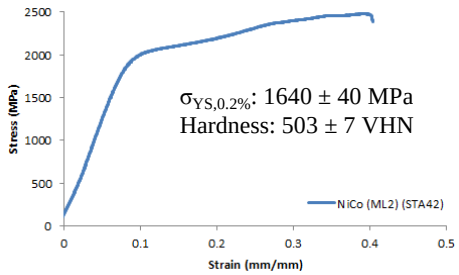
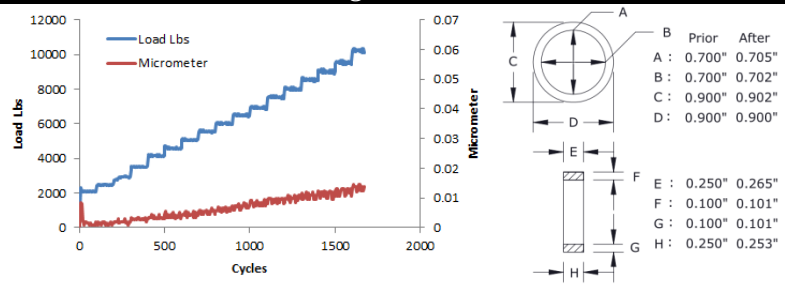
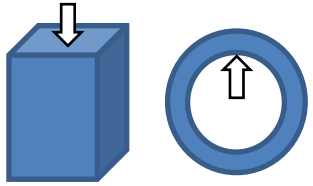
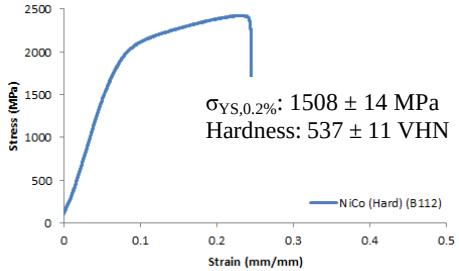
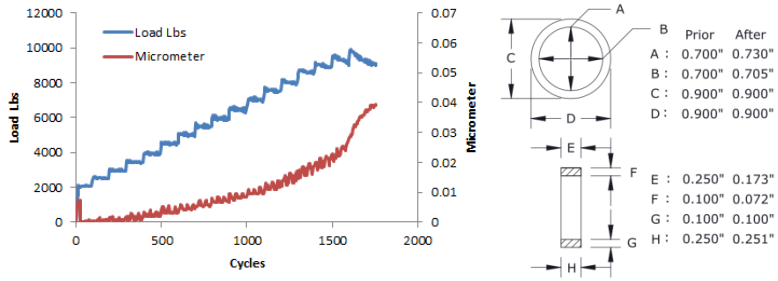
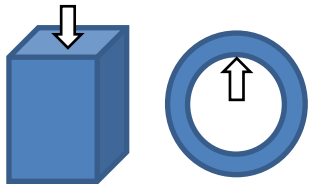
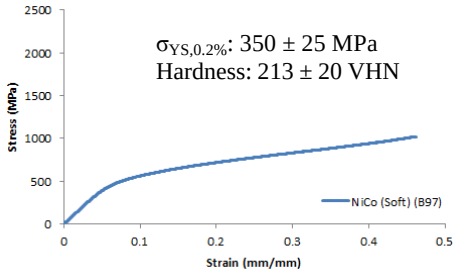
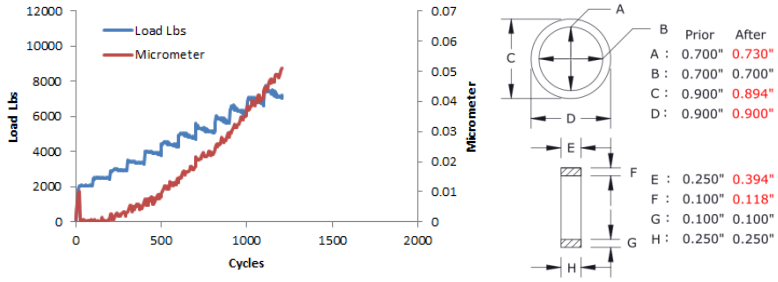
Figure 10: Summary of bushing test results for current and emerging CuBe-alternative materials (data from [6]).

Although there are many positives of the BioDur CCM (and ACUBE100) alloy, it has found limited use in the high-load bushing application because of its manufacturing process. In order to achieve its peak 0.2% yield strength of 1,117 MPa and hardness of 50 Rockwell C (AMS 5918), the material requires combined work hardening and precipitation hardening, which is difficult to achieve in large bushings over 2.5” in diameter.

Bushing performance of Integran’s nano Co alloy was also assessed qualitatively by Cradin Aerospace. It was described that the nano Co alloy bushings a) were extremely quiet during the testing, b) and indicated low friction-generated temperature during the testing. This suggests that the friction coefficient is low for the nano Co alloy, supporting the data in Section 4.3. This may enable lubricant-free bushings, a concept which is also of importance for aerospace and military markets.

Although the nano Co alloy bushings performed best of the down-selected nanomaterials, another meaningful result was found: microstructural engineering of “multi-layered” or “modulated” could also improve bushing performance consisting of nickel-based alloys. In specific, nanostructured nickel-cobalt bushings could be engineered to possess bushing performance very near that of CuBe, i.e., due to a multi-layering approach, performance summarized in Table 9. The monolithic nano NiCo (537 ± 11 HV) failed in a brittle manner at around 1,600 cycles (10,000 cycles); and the monolithic ‘ultra-fine’ grained nickel-cobalt (213 ± 20 HV) failed in a ductile manner from test start until stopped at ~1,200 cycles. However, by multi-layering these two deposit types, i.e., modulating the nanostructured and ‘ultra-fine’ grained microstructures using a single bath, a novel bushing was generated which could be loaded up to 10,000 lbs (1,670 cycles) with low deformation (most clearly shown by the lack of rapid increase in micrometer reading).

Table 9: Summary of bushing performance testing for Integran's nickel-cobalt alloy bushings.

	Sample Details (Schematic)	Compression Test Results	Bushing Test Results
NiCo (Alloy #3, ML)	Compression Bushing 		
NiCo (Nano)	Compression Bushing 		
NiCo (Ultra-Fine)	Compression Bushing 		

5.4 SCALE-UP OF BUSHING MANUFACTURE

Section 2.1.1 has described in detail the benefits and overall approach Integran proposes for scaled-up bushing manufacture, i.e., via an electroforming approach. In short, this approach a) makes use of the processing flexibility of electrodeposition, b) has been demonstrated as cost-effective for other industries, and c) produces a near-net bulk shape resulting in less material waste and a very high buy-to-fly ratio. A schematic of the approach for bushing manufacture is illustrated in Figure 11. Also in Figure 11 is a picture taken of 7 different sizes of nanostructured metal bushings machined to pseudo-standard ID/OD dimensions, all of which were *manufactured simultaneously from a single mandrel*.

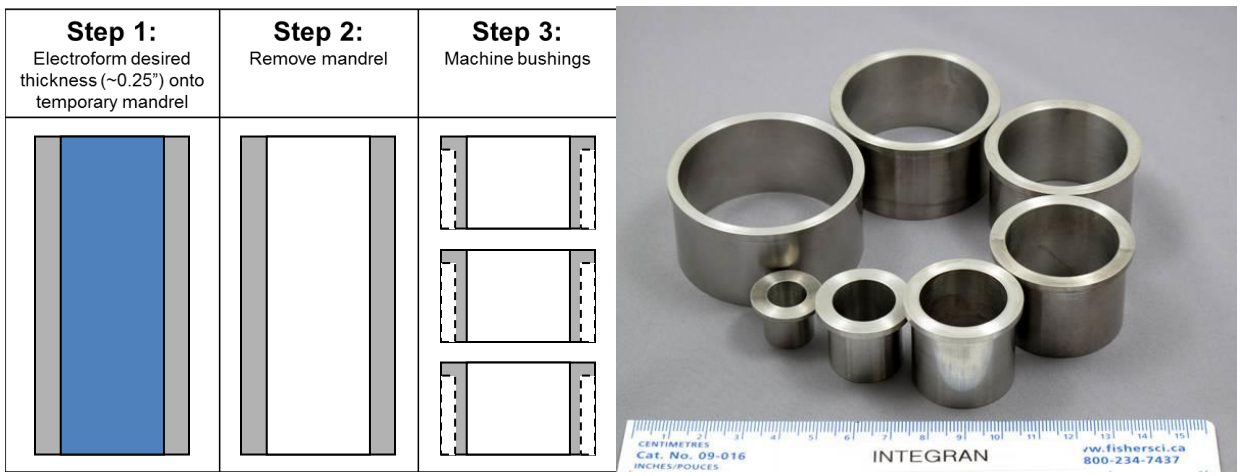


Figure 11: Manufacturing and flexibility of nanostructured metal bushings.

When considering the cost of the bulk bushing material (the fraction of material waste is generally on the order of 80-95% depending on bushing geometry), combined with the high bulk cost of CuBe rod, and adding to that the cost of machining, the overall cost for the nanostructured metal bushings compares very close to that of CuBe, and likely is more cost effective as the bushing diameter increases.

6.0 TASK II-3 – NANOMETAL COMPOSITE HYBRID TESTING

6.1 TASK OBJECTIVES

This task primarily performed work to generate and test Nanometal-composite hybrid sheet as effective alternatives to CuBe sheet. Some test data supporting this concept was collected during Phase I which showed that: a) high adhesion could be reached in the form of peel strength between nanostructured metal and composite (after ASTM B533) of at least 25-30 N/cm; and b) the hybrid sheet with similar thickness to CuBe (1.25 mm versus 1.04 mm, respectively) performed *4× better in weight-specific bending strength and 6× better in weight-specific bending stiffness* than CuBe.

In addition, work was conducted with industry partners in order to evaluate Nanometal foil and thin-walled electroforms as alternatives to CuBe products. One example of this was identified in Phase I, i.e., freestanding

nanostructured foil as an alternative for CuBe foil for applications that require high fatigue performance with low electrical resistance. A second example of the latter was identified during Phase II. Namely, electroformed nickel alloy metal bellows were identified as an industrial product which has made some successes at replacing CuBe bellows. This is described further in 6.5.

In Phase II, additional tasks were executed. First, the manufacturing process was scaled-up to produce Nanometal-composite hybrids using off-the-shelf composite. In Phase I uniaxial-ply carbon-composite was used as the substrate; in order to represent multi-axis loaded parts, bi-directional 'twill' carbon-composite was selected in Phase II for the substrate. The details for this material are provided in Table 10.

Table 10: Average physical characteristics of composite material used in Phase II.

Weave	2×2 Twill
Yarn Type	T300B (Toray) 3K 40B
Count	13.0 × 12.7
Areal Weight	201.3 g/m^2
Thickness	0.014 inches (0.36 mm)
Resin Content	40-44% UF3376 TCR™ Resin

Panels were manufactured in areas of at least 9"×8" in order to generate test samples for mechanical performance evaluation against CuBe, including ASTM D790 (three-point bending), ASTM D7136 (impact), and ASTM B593 (flexural fatigue). Samples were treated on one side with Intebond™ for adhesion followed by plating. Flexural fatigue testing was also conducted following ASTM B593 for stand-alone nanostructured metal platforms. Also as part of this task, Nanometal electroformed bellows were manufactured and tested as a potential alternative to hydroformed CuBe bellows. Integran worked with Servometer (Cedar Grove, NJ) to evaluate bellows manufactured from nanostructured metals.

6.2 THREE-POINT BEND TESTING OF NANOMETAL/COMPOSITE SHEET HYBRIDS

6.2.1 Panel Manufacture and Adhesion Testing

In this Phase, panels of sizes 9"×8" were manufactured using the 3K 2×2 Twill composite, layed-up and cured. A Nanometal/composite sheet hybrid thickness of ~1.0 mm was targeted to be closer to that of the CuBe sheet tested in Phase I. This consisted of a cured composite thickness of 0.92 mm, a thickness of 50-150 μm of Integran's Intebond™ adhesion primer film co-cured on one side of the composite, and a thickness of ~50 microns mass-average of nano NiCo alloy applied to the Intebond™ surface. This generated a Nanometal/composite hybrid with thickness of 1.1 mm, shown in Figure 12 with cross-section.

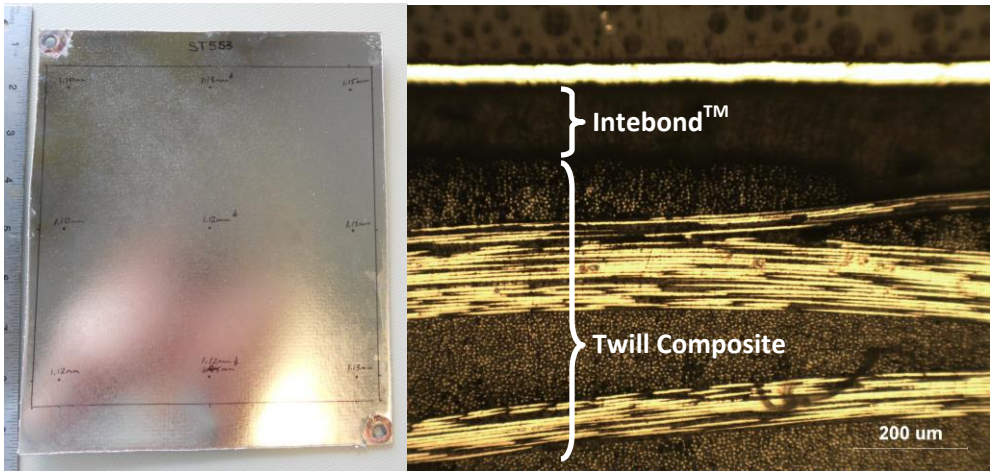


Figure 12: Nanometal/composite sheet hybrids and cross-section manufactured in Phase II.

As was performed in Phase I, Integran's proprietary Intebond™ technology was applied to the substrate in all cases in order to improve the metal-to-composite bond strength and thereby enabling the nanostructured metal to provide added structural reinforcement. The peel strength between the nano NiCo and the 3K 2×2 Twill composite panel was confirmed similar to that in Phase I after ASTM B533.

6.2.2 ASTM D790 Bend Testing of Nanometal/Composite Sheet Hybrids

As in Phase I, in three-point bend loading, significant increases could be achieved in the present hybrid over the CuBe benchmark. Again, the overall bending performance of the hybrid sheets is largely defined by the modulus and tensile strength of the fibers (the latter typically 2× larger than that for CuBe) combined with the resin percentage. As was done in Phase I, Nanometal/composite samples (generated using the twill material) were tested in three-point bending and compared against CuBe using known weight-specific material indices [23] i.e., optimizing panel and beam products under bending load with minimal mass. A summary of the material indices is shown in Table 11.

Table 11: Material indices used to evaluate Nanometal/Composite hybrids vs. CuBe in bending (from [23]).

Description	Example Application	Index
Beam, minimum weight, stiffness prescribed	Aircraft wing spar, golf club shaft	$E^{1/2}/\rho$
Panel, minimum weight, stiffness prescribed	Car door panel	$E^{1/3}/\rho$
Beam, minimum weight, strength prescribed	Suspension arm of car	$\sigma^{2/3}/\rho$
Panel, minimum weight, strength prescribed	Table top	$\sigma^{1/2}/\rho$

As was shown in Phase I, the Phase II results showed that the hybrid sheet performed better than CuBe. In specific, it was found that at nearly-equal thickness, the hybrid sheet using the twill composite performed *3× better in both weight-specific bending strength and weight-specific bending stiffness* than CuBe (Figure 13).

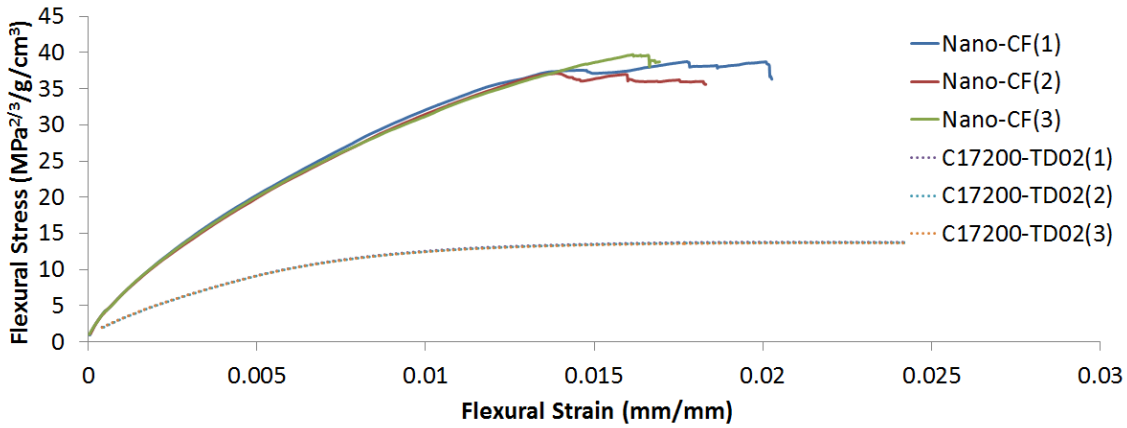


Figure 13: Flexural stress versus strain data. Stress has been normalized by index $\sigma^{2/3}/\rho$ (see text).

In Phase I, it was found that the hybrid sheet performed better than CuBe by up to factors of 4 and 6, respectively, for strength and stiffness. It is expected this was due in part to a) the increased sample thickness in Phase I (1.25 mm) and b) uniaxial composite fiber orientation in Phase I compared to 2×2 Twill in Phase II. Uni-directional laminated carbon composites are rarely used due to their highly an-isotropic properties, a quasi-isotropic lay-up (such as twill) is more applicable to general product forms where more isotropic properties (and improvements over CuBe) are required.

CuBe sheet is currently used in a number of product forms. Some of these product forms depend on CuBe's high specific strength and stiffness which lends to high performance in flexural loading. DoD and industry-relevant applications of this product form include leaf springs (e.g., [24]) and disc springs/Belleville washers (e.g., [25]). CuBe's high fatigue strength, corrosion resistance, conductivity, and galling resistance, among other characteristics, also make it an ideal choice for these applications. In other product forms, the precision stamp-ability and cast-ability of CuBe allows it to be fabricated into very thin and therefore highly sensitive pressure gauges, diaphragms, bellows, gaskets, 'finger strips', and contact springs, many of which are DoD- and industry-relevant. CuBe's high fatigue strength, thermal and electrical conductivity, high-frequency EMI shielding, corrosion resistance, and dimensional stability (e.g., zero stress relaxation under loading at elevated temperatures), among other properties, also make it an ideal choice for these applications. A third group of product forms (not the specific focus of this program) also relies on the precision cast-ability and high heat conductivity of CuBe, such as inlet guide vanes for helicopter turbines.

6.3 ASTM D7136 DROP-WEIGHT IMPACT TESTING

Three-point bend samples manufactured in Section 6.2.1 were also exposed to drop-weight impact testing prior to three-point bending. Testing was performed using an in-house drop-weight set-up at Integran, shown in Figure 14. The indenter tip shown in Figure 14 with hemispherical geometry was modeled after that outlined in ASTM D7136, "Measuring the Damage Resistance of a Fiber-Reinforced Polymer Matrix Composite to a Drop-Weight Impact Event". Samples with and without Nanometal were exposed to increasing amounts of impact energy up to 9.0 J, and the resulting three-point bend performance was measured. (A similar methodology was implemented for fatigue testing after impact, Section 6.4.)

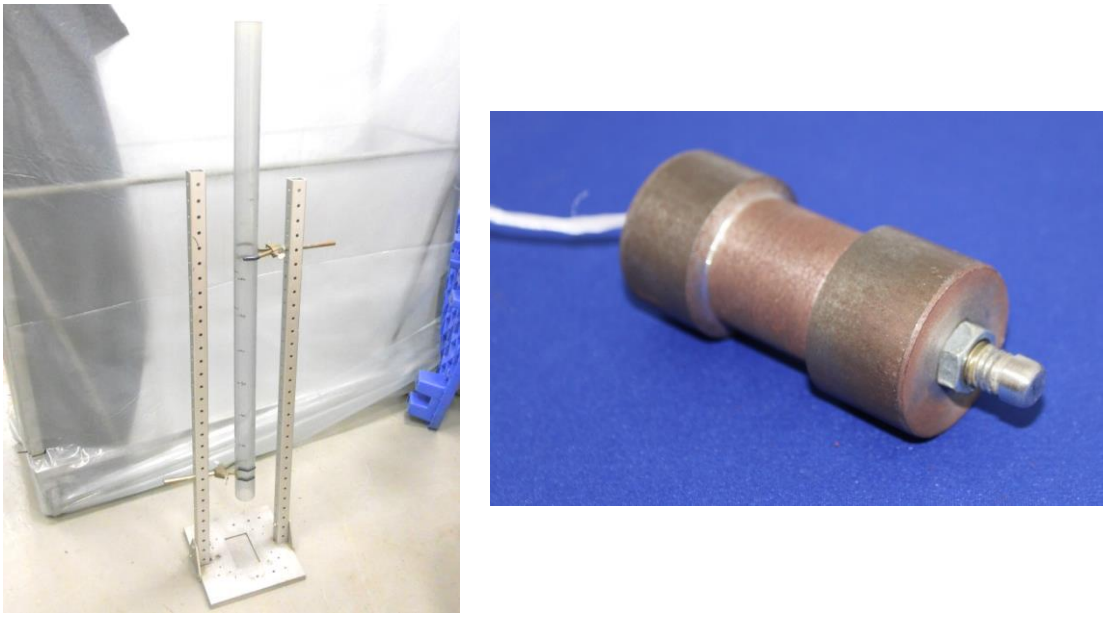


Figure 14: Drop-weight impact tester (and weight) internal to Integran.

Test results showed that even after 9.0 J (0.61 kg from 1.5 m height) of impact energy imparted to the hybrid sheet (the maximum capable by this set-up), there was no statistically significant change in bend strength or stiffness (or weight-specific material indices) following impact for either the Nanometal/composite or composite-only samples. This suggests a level of durability in the hybrid while also maintaining the performance advantage over CuBe.

Table 12: Summary of bend test data (with and without impact).

	$E^{1/2}/\rho$	$E^{1/3}/\rho$	$\sigma^{2/3}/\rho$	$\sigma^{1/2}/\rho$
	$MPa^{1/2}/g/cm^3$	$MPa^{1/3}/g/cm^3$	$MPa^{2/3}/g/cm^3$	$MPa^{1/2}/g/cm^3$
CuBe (C17200-TD02)	43.9 ± 0.1	6.2 ± 0.0	13.7 ± 0.1	4.2 ± 0.0
Nano-CF (no impact)	120.5 ± 1.5	21.2 ± 0.2	38.5 ± 2.8	13.9 ± 0.4
Nano-CF (impact)	120.3 ± 1.0	20.8 ± 0.2	35.6 ± 4.2	12.9 ± 1.1

6.4 ASTM B593 FLEXURAL FATIGUE TESTING

A four-sample flexural fatigue testing machine was used (refer to [26]) to test materials after the ASTM B593 standard. Samples were manufactured similar to Section 6.2.1, fitted to the test sample configuration and geometry for this machine. Shown in Figure 15 is a schematic of the test sample configuration (as per the machine supplier) as well as an image of coated and un-coated samples. The length dimension and thickness were selected to match the target loads. Samples were cut via water-jet, which resulted in some surface roughness (which was later reduced via mechanical sanding). For the Nanometal-composite hybrids, the water jet was oriented to first strike the metal surface for improved sharpness. Water jet cutting did not result in delamination between the Nanometal and the composite (see top sample in Figure 15).

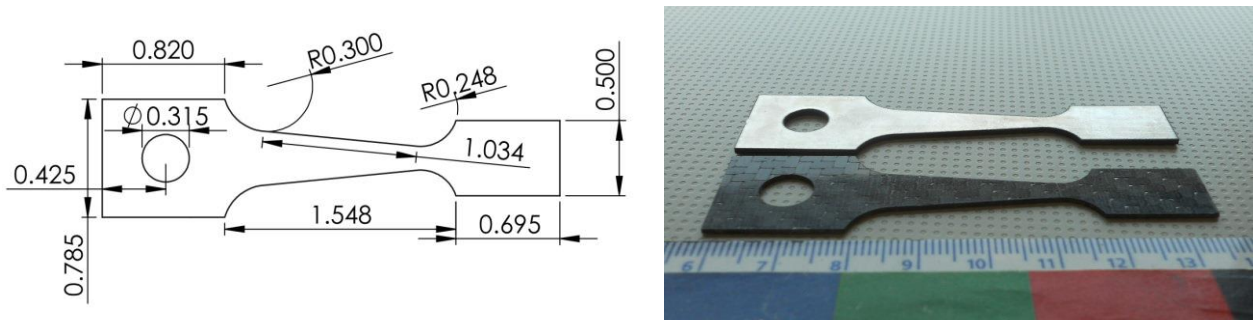


Figure 15: Test sample dimensions (left) and manufactured test samples (right) for ASTM B593 testing.

Flexural fatigue data for CuBe (C17200 TH04 i.e., AMS 4534) following the ASTM B593 standard has been published in ASM Handbooks [27] at a cycle frequency of 15-25 Hz. The data for this alloy in the R = –1 condition (i.e., full forward and reverse bending) is reproduced from this reference and compared against layed-up composite material, also tested at a cycle frequency of 15-25 Hz. Shown in Figure 16, at a stress of ~360 MPa (R = –1), the composite material was tested up to 2.3×10^6 cycles with no loss in load-carrying capacity (the test was stopped at 2.3×10^6 cycles due to time limitations; and a stress of 360 MPa was the maximum for this sample geometry). This is at least as long as the CuBe C17200 TH04 material. Testing was also performed on Integran's nano NiCo alloy at the same and higher stresses (365, 550, 700, and 840 MPa). Shown in the figure, the fatigue strength of Integran's nanostructured material matches that for the CuBe. Additional testing could not be performed due to time limitations. However, the data collected suggests that the fatigue strength of Integran's nanostructured material and carbon fiber composite is at least as high as CuBe alloys. Based on this, it is believed that the fatigue performance of Nanometal/composite hybrids would be at least that of CuBe alloys. The *weight-specific* fatigue strength would therefore far surpass that for CuBe.

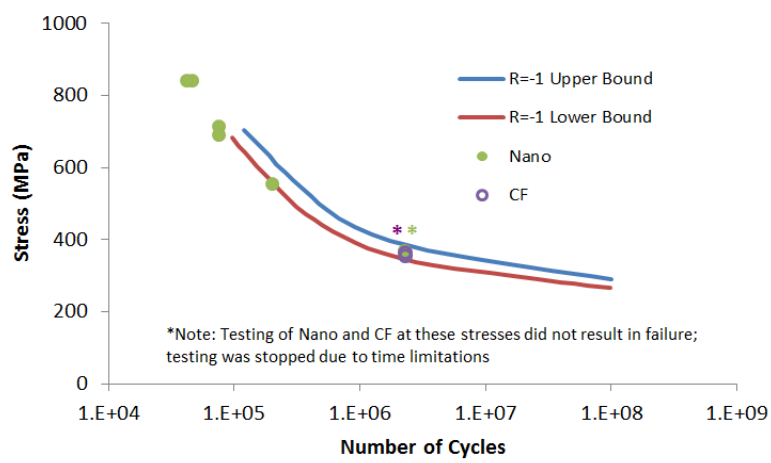


Figure 16: Flexural fatigue of CuBe (C17200, TH04 temper) versus materials generated by Integran.

Also of relevance when discussing strip applications requiring high fatigue strength and resilience is the material's modulus of resilience, i.e., ratio of yield strength to elastic modulus. For CuBe alloys, their high modulus of resilience has resulted in the use of CuBe alloys as switches, electromechanical relays, fingers, and

other similar applications. However, as shown in Table 13, Integran's nanostructured materials (particularly nano NiCo and nano Co alloy) compare favorably in terms of resilience and can even surpass that of CuBe. When the nanostructured materials are added to carbon fiber composite, the modulus of resilience is expected to be further improved and can be maintained even following damage events.

Table 13: Modulus of resilience for CuBe alloys and Integran's nano NiCo and nano Co alloy.

Material	Standards	0.2% Yield Strength	Elastic Modulus	Modulus of Resilience	Reference
C17200-TF00	ASTM B194 QQ-C-533	960-1,210 MPa	131 GPa	$7.3\times10^{-3} – 9.2\times10^{-3}$	Matweb
C17200-TH04	ASTM B194 QQ-C-533	1,130-1,420 MPa	131 GPa	$8.6\times10^{-3} – 10.8\times10^{-3}$	Matweb
C17510-TH04	ASTM B534 RWMA 3	650-830 MPa	138 GPa	$4.7\times10^{-3} – 6.0\times10^{-3}$	Matweb
Nano NiCo	n/a	~1,017 MPa	~145 GPa	$\sim7.1\times10^{-3}$	(in-house)
Nano Co alloy	n/a	1,601 MPa	130 GPa	$\sim12.3\times10^{-3}$	(in-house)
T300 Composite	n/a	1,470-1,860 MPa	125-135 GPa	$11.8\times10^{-3} – 13.8\times10^{-3}$	[28]

*Modulus of Resilience is reported as $\sim7.0\times10^{-3}$ for C17200-TF00 and $\sim8.2\times10^{-3}$ for C17200-TH04 in [27].
*Values for Integran's materials are approximate.
*Matweb reference is www.matweb.com

6.5 ELECTROFORMED NANOSTRUCTURED METAL BELLOWS

6.5.1 General Introduction

Metal bellows are flexible linkages which can be deformed upon the application of vacuum or other pressures. These components possess a number of applications, including: load cells, vacuum interrupters, mechanical seals, pressure gauges, sensors, valve seals, couplings for stepper motors and servomotors, exhaust bellows, and expansion joints. Because these bellows typically experience repeated and sometimes high-load deflection, high strength and high fatigue life are critical. As outlined in Section 6.4, these characteristics are met well by CuBe alloys.

Standard polycrystalline electroformed metal bellows are commercially available as an alternative to CuBe bellows. In this case, the benefits are two-fold. First, the toxic elements of beryllium are effectively replaced. The second benefit makes use of the fundamental process differences. While CuBe bellows are produced by hydroforming, this process possesses limitations in wall thickness, bellows geometry, and overall wall thickness uniformity. On the other hand, electroforming is a process which enables more uniform, thin-walled, and smaller precision bellows, which consequently enables improved sensitivities to pressure. However, conventional electroformed bellows consist of *polycrystalline* nickel alloy. In this task, work was also performed to evaluate the potential improvements of electroformed metal bellows (as replacements to CuBe bellows) consisting of *nanocrystalline* materials.

6.5.2 Testbed Selection

Conventional bellows are manufactured commercially by Servometer (Cedar Grove, NJ) among other companies. The electroforming process enables a high degree of flexibility with respect to geometry and wall thickness. An example range of products is shown in Servometer's online catalogue [29]. The manufacturing

process for the bellows follows a conventional electroforming operation with sacrificial/consumable aluminum mandrel (refer to [29]).

The mechanical properties of Servometer's electrodeposited nickel alloy are [29]:

- Yield strength: 110 ksi (758 MPa);
- Tensile strength: 125 ksi (862 MPa);
- Elongation: 1.0%
- Hardness: 270 Vickers

It is anticipated that increases in strength, hardness, and elongation of Integran's nanostructured metals and alloys (e.g., nano NiCo, Table 4), as well as fatigue strength, torsion strength, and corrosion resistance – all of which Integran's nanostructured metals offer – may lead to improved bellows products.

To evaluate Integran's nanostructured materials as bellows, the Servometer "FC-15" bellows geometry was selected as a testbed due to it being commercially available for benchmark testing.

6.5.3 Integran Bellows Manufacture

Using Integran's nano NiCo alloy system, applied to the processing methods familiar to Servometer, a number of bellows were produced and sent to Servometer for testing. Via cross-section measurements, it was confirmed that Integran's process could be able to reach the dimensions required by Servometer (specifically, ratio of thickness between the convolution peaks and valleys) for their commercial products. Figure 17 shows an example plated mandrel before and after chemical removal of the mandrel (i.e., the final bellows product).

Figure 17: Example plated bellows mandrel before (left) and after (right) mandrel removal.

6.5.4 Integran Bellows Testing

Prior to Servometer's evaluation, a single electroformed bellows mandrel was generated for internal compression testing at Integran. In this case, the mandrel was removed chemically and the resultant bellows was tested in compression to evaluate the load-deflection characteristics. In addition, a standard FC-15 bellows consisting of Servometer's nickel alloy was tested for comparison.

To evaluate the influence of the higher strength and hardness in the nano NiCo bellows over the FC-15 bellows, both were compressed to a level of 15% of the pressure rating (Figure 18). (Note: the wall thickness

of the trial nano NiCo bellows manufactured by Integran was 0.0029", less than the nominal 0.0035" for the FC-15. This accounts for the decreased load at 15% in the nano NiCo bellows.) For the nano NiCo bellows, both the loading (blue) and un-loading (red) curves virtually overlapped with permanent deformation on the order of 30 microns (0.001") over the ~3 cm total length, equivalent to a plastic strain of ~0.1%. In contrast, for the FC-15 bellows, there was a permanent deformation of ~1.2 mm – a factor of 40× greater than for the nano NiCo bellows.

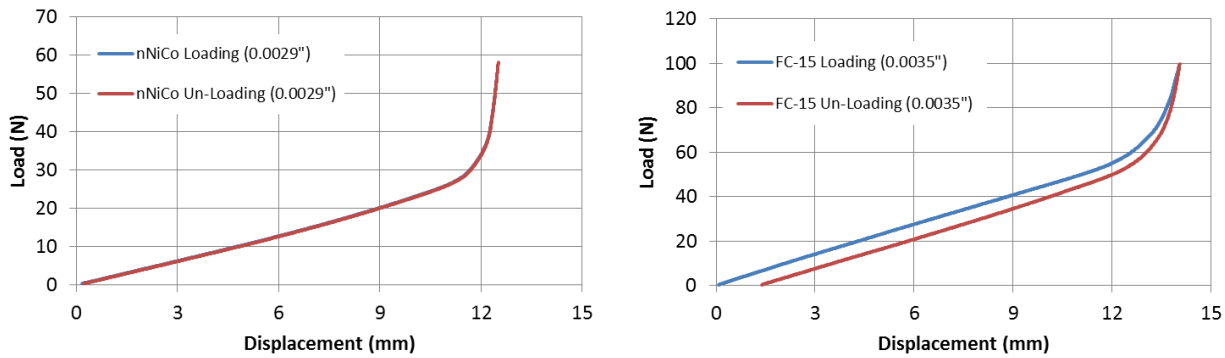


Figure 18: Integran compression testing of nano NiCo and FC-15 bellows.

In addition, from Figure 18 the Spring Rate (load/displacement) was calculated and compared to the design-defined values (e.g., [29]). This parameter is a defining factor for bellows: lower spring rates are more desirable as they are more sensitive to loading. For the two bellows, the average up to 5% of the Pressure Rating was measured as 2.23 N/mm (for nano NiCo) and 4.92 N/mm (for FC-15). Both values were within their respective ±30% design tolerance as targeted by Servometer.

One of the primary value propositions offered by electroformed bellows over CuBe hydroformed bellows is sensitivity in the form of spring rate. The performance of the FC-15 and nano NiCo bellows can be compared to equivalent bellows commercially manufactured from CuBe e.g., from Sigma-Netics (Fairfield, NJ) [30] and from Mini-Flex (Ventura, CA). While CuBe bellows are made via hydroforming, electroformed bellows will be able to reach thinner walls and 'ultra-low' spring rates compared to hydroformed bellows, so long as the constituent metal is capable of maintaining its shape. For example, Servometer does offer bellows with wall thickness down to 0.0005" (13 µm). These products require the highest material performance. The higher hardness of the nano NiCo bellows (537 ± 11 HV, Table 4), versus 270 HV [29]) and modulus of resilience and fatigue strength (Table 13), contributes to a theoretically improved bellows over the existing commercial products made from CuBe alternatives.

6.5.5 Servometer Bellows Testing

More detailed mechanical testing of the electroformed bellows was performed by Servometer using facility equipment. In order to do this, plated mandrels were sent to Servometer for chemical removal of the mandrel. Final bellows were inspected visually by the more experienced Servometer staff. Following inspection, bellows were then tested by Servometer for a combination of spring rate, compressibility, compression fatigue, integration with couplings, helium retention, and torque capacity.

In general, Servometer's bellows testing showed that bellows manufactured with Integran's nanostructured

materials performed similar to Servometer's 'standard' FC-15 bellows.

In a spring rate test, bellows were compressed to 50% of their full rated compressive displacement. Integran's nano NiCo bellows met Servometer's ±30% spring rate tolerance relative to the designed values.

In a helium leak test[1], Servometer applied a thin flash of gold (via sputtering) over the ID and OD surfaces of the nano NiCo bellows. Leak testing showed that these bellows could reach a pressure of 1×10^{-9} cc He/second under vacuum and could prevent helium leakage. Subsequent fatigue testing of these bellows was performed to determine the quality of helium leak retention following cyclic compression (to 50% of the stroke rating). These bellows reached 250,000 cycles without deterioration of the helium leak retention or spring rate.

In a coupling torque test, couplings were joined via soldering to the outside faces of the bellows (a common product arrangement of Servometer). Torque tests were performed to see if a higher ultimate torque could be applied to the nanostructured metal bellows without failure. It was found that the nano NiCo bellows could reach an ultimate torque capacity of up to 50% greater than that of the standard Servometer bellows.

In summary, bellows consisting of Integran's nanostructured nickel-cobalt alloy (compared to polycrystalline nickel alloy) have showed higher compressibility without permanent deformation, good spring rate retention following cyclic loading, and can even undergo up to 50% higher stresses in torqueing.

7.0 TASK II-4 – NANOMETAL-ENABLED STRANDED WIRE TESTING

7.1 TASK OBJECTIVES

CuBe wire is currently manufactured for aerospace, medical, and electronics applications which utilize the material's high tensile strength-to-weight ratio, moderate electrical conductivity, superior flexural/fatigue life, and, in some cases, draw-ability (i.e., to manufacture wire with higher AWG from those with lower AWG). The overall objective of this task is to evaluate whether Nanometal-coated conductor wire may offer at least equal performance characteristics.

In Phase I, Integran demonstrated the ability to continuously produce Nanometal-enabled conductor wire using a number of copper wire substrates. That work showed that Nanometal-coated wire could be fabricated in batches of 500 feet. Via electrical resistivity measurements of other Nanometal-coated conductor wire, it was found that a 0.6% percent variation in wire conductivity could be achieved within a 500 foot length. Via tensile test measurements of the same wire, it was found that the tensile properties varied more considerably. This was believed to be due to the effect of defects in the wire substrate, which are magnified at smaller wire gauges, and which are expected to be more common with 'lower-grade' copper conductor wire. This was supported by plating a larger gauge wire, in which the goal of high tensile strength (>1,000 MPa) and good ductility (>5%) was reached.

In Phase II, work has focused on I) the acquisition of 'higher-grade' copper conductor wire and II) the plating

1 In the "helium leak test", bellows are exposed to a vacuum pressure followed by injection of helium. A probe is placed around the bellows to detect leaking helium. This is a critical application test as the majority of Servometer's bellows require leak tightness.

of this conductor wire with a nano Co alloy to match or exceed existing commercial CuBe wire products. As part of this task, Integran engaged with commercial partner IWG High Performance Conductors, Inc. (IWG-HPC) in Inman SC, who offer high-quality copper wire and copper alloy wire including CuBe wire. An example of IWG-HPC's CuBe wire is their CS-95® (UNS C17510) wire product with properties in Table 14, data from IWG-HPC's on-line catalogue [31].

Table 14: Summary of properties for an example commercial CuBe conductor wire (data from IWG-HPC).

	"Soft Temper" CS-95®	"Hard Temper" CS-95®
Elongation, min	6%	1%
Tensile Strength, min	655 MPa (95 ksi)	897 MPa (130 ksi)
Electrical Conductivity	63% IACS	40% IACS

In addition to the base CuBe wire offered by IWG-HPC, in some cases (e.g., CS-95®) coatings of silver (ASTM B298) and/or nickel (ASTM B355) are added to the CuBe wire for increased corrosion protection – but at a slight cost of decreased weight-specific strength. The Integran CuBe-alternative wire may be a further improvement as a nano Co alloy-plated wire will not require these additional coatings. In addition to CuBe wire, IWG-HPC also supplies large volumes of other copper alloy wire used extensively in the military and aerospace landscape. One such product is their Tensile-Flex® 135 (UNS C18135), which is a copper-chromium-cadmium alloy wire (0.2-0.6% Cr, 0.2-0.6% Cd).

In Phase I, Integran was in discussions with the wire/cable company IWG-HPC with the goal of developing a joint test plan for stranded wire testing. IWG-HPC agreed to execute stranding and testing/validation (as in-kind contribution) of the Nanometal-enabled conductor if Integran can provide enough material for the tests. The objective of this task was to manufacture sufficient wire length for the purpose of stranding by IWG-HPC into a 24 gauge wire product: 24 AWG 19/36, i.e., 19 strands of 36 AWG forming an equivalent 24 AWG stranded wire. As part of the test plan, IWG-HPC was to perform testing of the stranded wire including tensile strength, electrical resistance, and flexural fatigue, among other tests.

7.2 RESULTS

7.2.1 Manufacture of Wire for Testing

For the scale-up of Nanometal-enabled conductor wire, IWG-HPC provided Integran a number of spools of soft copper conductor wire (38 AWG) substrate, each spool containing ~2,000 feet. This wire length was selected as 1,500 feet is the minimum length to run through IWG-HPC's stranding machine; and it was expected there would be some wire loss due to spool set-up in and take-down from the wire line. In order to generate the Nanometal-enabled conductor wire, a few modifications were required for spooling, i.e., to mate Integran's plating equipment with the spools provided by IWG-HPC. In addition, insulation was added to the plating set-up to prevent any heat losses over the semi-continuous plating of 2,000 foot spools.

Shown in Figure 19 and compared to Phase I, this wire appeared to be much more defect-free. In addition, the hardness of the substrate conductor wire was ~80 HV_{25}, unchanged after plating. The cross-section diameter (measured in-house by Integran) was approximately 101-102 μm, which is in-line with the standard 38 AWG wire diameter. The final wire diameter of 130 ± 1 μm was in-line with the standard gauge for 36 AWG wire.

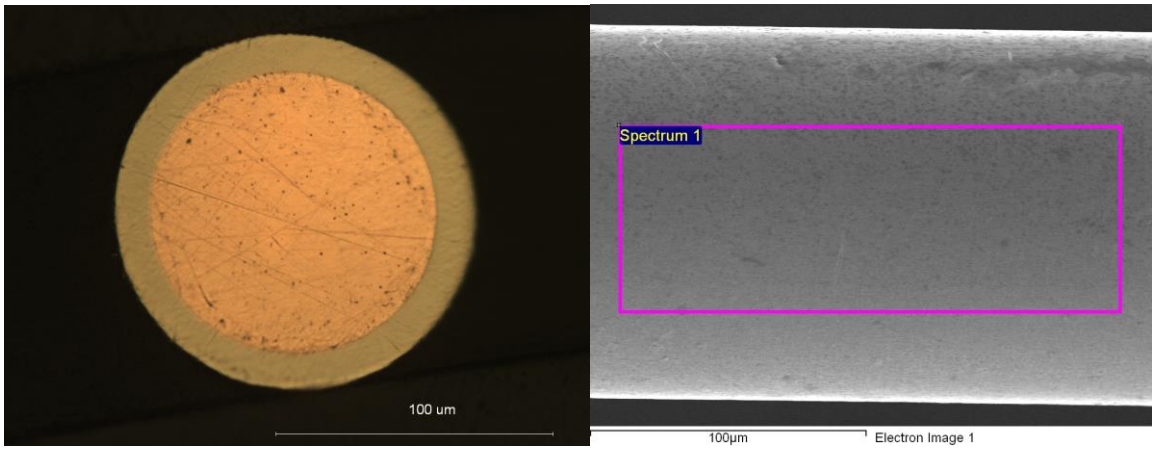


Figure 19: Images of the Nanometal-enabled conductor wire following plating.

The results of Integran's in-house wire testing are summarized in Table 15. The overall performance shows that the wire possessed the strength of the "Hard-Temper" CS-95® wire and conductivity of the "Soft-Temper" CS-95® wire, and ductility between the two tempers. It was found that the tensile strength and electrical conductivity both scale as expected using a rule-of-mixtures model. Furthermore, the wire possessed good bending ductility, represented by winding around a steel mandrel with diameter 5 mm (Figure 20).

Table 15: Summary of properties of Nanometal-enabled conductor wire (data in-house at Integran).

Electrical resistivity	60-70% IACS
Cross-section area	130 ± 1 µm
Tensile strength	895 ± 57 MPa
Tensile ductility	6.1 ± 2.5%

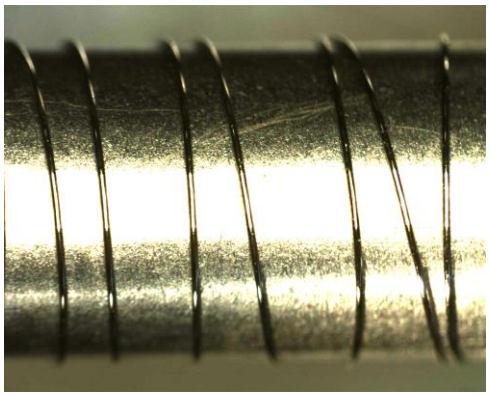


Figure 20: Bend-ability testing of the Nanometal enabled conductor wire around a 5 mm diameter steel mandrel.

However, as was experienced during Phase I of this project, the average ductility of the Nanometal-enabled conductor wire was lower than expected, reduced by a non-trivial variation in ductility. In order to investigate

more closely the source of this variation, fracture surfaces of the wire were investigated by scanning electron microscope (SEM). A cross-section of a wire tensile-tested to failure demonstrates high adhesion between the copper core and the Nanometal sleeve (Figure 21). Inspection of the fracture surface in the nanostructured metal coating shows successful 'multi-layering' (B) which was sought after at the outset of the project; this fracture contrasts sharply with the classical ductile fracture surface morphology within the copper core. However, visible in the fracture surface there are small defects at the coated wire surface (C) which appear to be from where fracture originates. A side profile of the wire (D) shows other defects present at the surface of the coated wire.

The multi-layering induced into the coating, combined with the application of nanostructured metal to conventional wire plating, is considerably different from conventional wire plating. It was not certain what effect these defects would have on the overall wire stranding/testing.

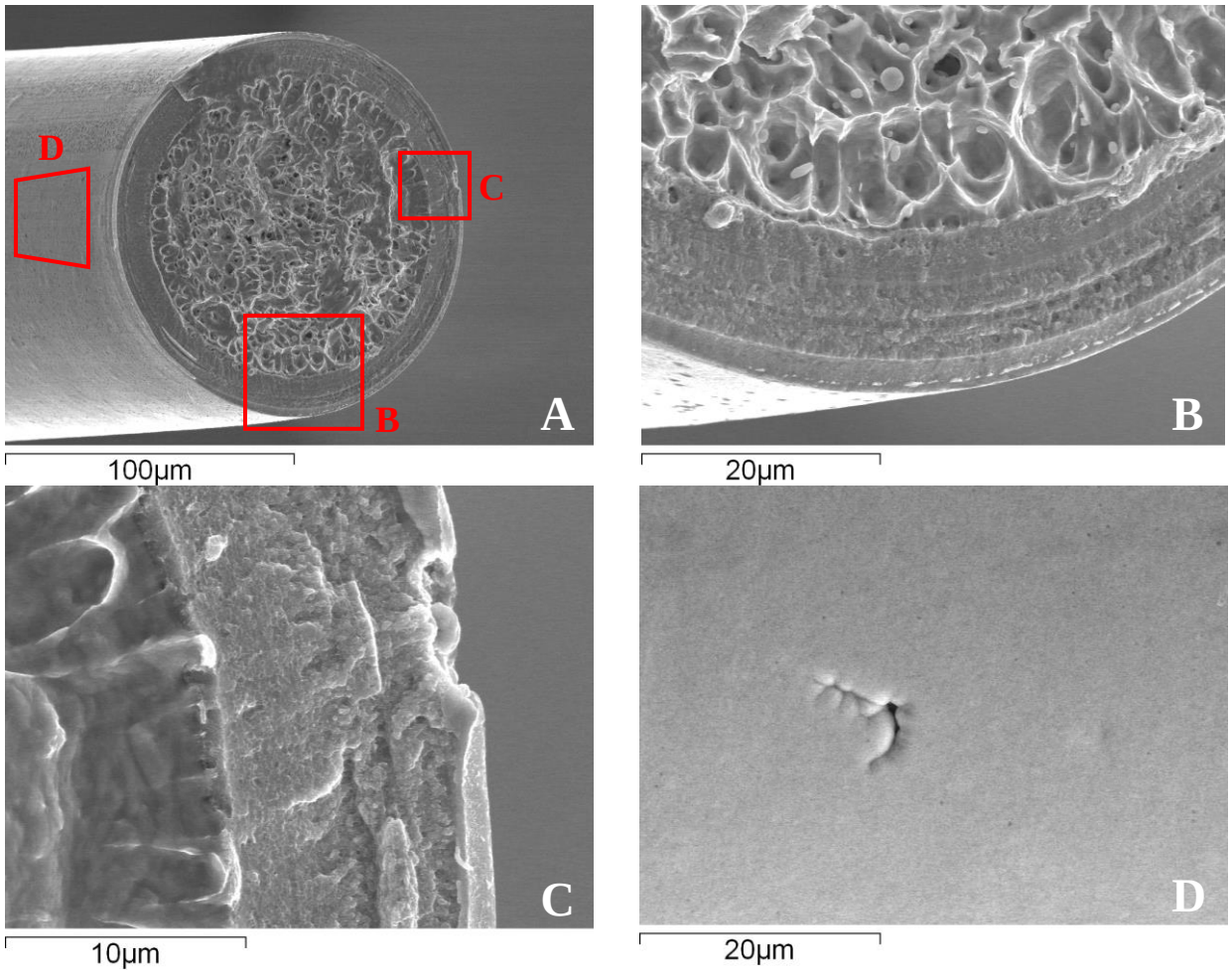


Figure 21: Images of Nanometal-enabled conductor wire tensile-tested to failure.

7.2.2 Evaluation of Wire for Commercial Testing

Integran successfully manufactured 19 spools of 1,500+ feet each (a total of 28,500+ feet) to IWG-HPC,

shown in Figure 22. This section includes the evaluation of the wire by IWG-HPC.

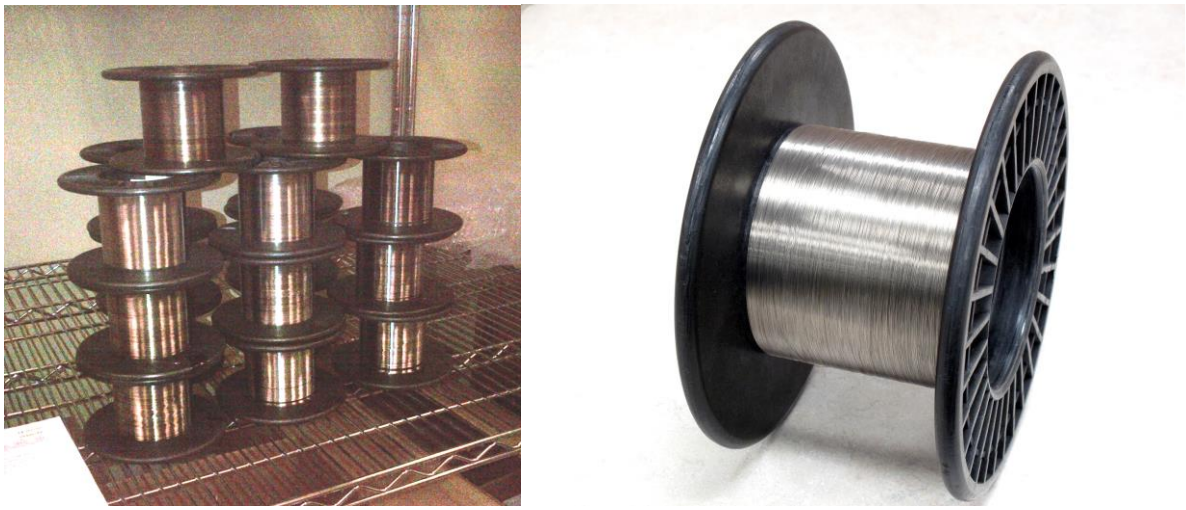


Figure 22: Spools of Nanometal-enabled conductor wire (each spool 1,500+ feet) sent to IWG-HPC.

Individually-tested single strands of wire displayed significantly higher tensile results than IWG expected from "normal" nickel plated 36 gauge wire. The average tensile strength (two strands) measured by IWG was ~125 ksi (860 MPa); and the average electrical conductivity was 69.2% IACS. The values obtained from IWG-HPC are similar to those obtained by Integran in-house (Table 15). Again with reference to Table 14, the strength is similar to that expected from the "Hard Temper" CS-95®, while the electrical resistivity is similar to that expected from the "Soft Temper" CS-95®. This would enable a value proposition in applications where either current-carrying capacity or strength is a limiting factor. For comparison purposes, soft 36 gauge nickel-plated copper wire has a tensile strength of approximately 36 ksi (~250 MPa) and a conductivity of ~98% IACS. In addition, this result confirms that conductor wire consisting of nanostructured metal coating and a copper core may be designed following a rule of mixtures.

However, difficulties were discovered by IWG-HPC when stranding. It was found that Integran's Nanometal-enabled conductor wire would break during installation in the stranding mandrels – the smallest of which were communicated by IWG to be on the order of ~3/4" (19 mm) [32]. This breakage appeared to contrast the results from Integran's bend-ability testing (Figure 20) which showed the wire could be wound around a 5 mm diameter without fracture (a strain of ~1.3%). It is believed that this result was due to one of two issues: 1) stranding exposed the wire to combined bending and tension, exceeding the wire's capacity, or 2) within the 10-foot length required by IWG-HPC to mount in the stranding equipment, there was a critical defect which limited ductility. Repeated efforts by IWG-HPC did not result in successful stranding.

Because the nano Co alloy-coated copper conductor wire could not be stranded, the remaining tests requiring stranded wire could not be performed.

Of the wire tests performed by IWG-HPC, one of the most influential in terms of value determination is the flexural fatigue test (as per ASTM B470). In this test, stranded wire is placed in a metronome-like apparatus

and bent from the vertical in a ±60° set-up around a mandrel of specific radius. The CS-95® CuBe wire typically reaches 6,000-8,000 flexes before failure [32]. Based on the relative flexural fatigue life (ASTM B593) of Integran's nanostructured metals versus CuBe (UNS C17200) (Section 6.4) and data in Table 13, it is anticipated that Nanometal-enabled conductor wire would possess improvements over CuBe wire. ASTM B593 fatigue performance has also been collected for C17510 alloy strip (TH04 temper) [27], which is similar to the CS-95® wire alloy. At a stress of ~435-485 MPa, C17510-TH04 fails after 10^5 cycles, whereas at that same number of cycles Integran's nano NiCo alloy can be cyclically loaded up to ~680 MPa before failure (Figure 16). At a stress of ~325-375 MPa, C17510-TH04 fails after 10^6 cycles, whereas Integran's nano NiCo could be cyclically loaded at 365 MPa without failure even after 2.3×10^6 cycles.

In addition to difficulties experienced during stranding, IWG-HPC also noted that the surface of the Nanometal-enabled conductor wire was rougher than typical for their CS-95® wire. This was not altogether surprising as there was no post-plate processing in the Integran wire. During commercial processing of wire which possesses a coating (e.g., of nickel), it is standard to *draw down the wire after plating*. By doing so, the surface roughness of the final wire is very low and defects are minimized, but also a high level of strain is introduced into the material. IWG-HPC noted that wire plated with standard nickel but without a post-drawing operation would have similar surface quality as the wire supplied by Integran [32].

Another reason for drawing after plating is economics. Via drawing after plating, it is less expensive and faster to make large volumes of wire. Currently, IWG-HPC supplies on the order of ~3,000 lbs (~1,360 kg) of CS-95® wire *per month* [32]. As CS-95® wire is predominantly a fine-gauge product, this monthly production equates to a linear production rate of ***~20,000 km*** (60 million+ feet) per month (using size 38 AWG as the model). While Integran's processes do possess high efficiencies and plating rates, matching this level of production would be difficult via plating on wire already drawn to the final dimension. Wire drawing was considered for the Nanometal-enabled conductor wire generated during this Phase, but the drawing process requires considerable ductility of the core and any surface coatings, and the drawing is typically conducted at elevated temperatures which would change the grain-refined microstructure of the Integran coating.

7.2.3 Summary and Alternative Wire Designs

Integran's nano Co alloy possesses exceptionally-high mechanical strength (e.g., Figure 2) which, when coated on copper conductor wire, enables the hybrid wire to reach tensile strength equivalent to high-strength CuBe wire (but with improved electrical conductivity). However, the Nanometal-enabled conductor wire would not be stranded, which currently limits it as a commercial product.

Despite this shortfall, there are additional avenues for development. For example, Integran possesses a number of alternative materials which possess increases in ductility over the nano Co alloy at a minor expense of strength. Nanostructured nickel-cobalt is one example: Using a rule-of-mixtures design approach, the hybrid strength of a Nanometal-enabled conductor wire is greater than the CS-95® "soft temper" with similar hybrid conductivity. *This is the more common temper in which the CS-95® is sold by IWG-HPC, as many military and aerospace applications require wire with 6% minimum elongation* [32]. A hybrid wire of this kind would also possess break strength higher than standard ultra-high strength alloy conductor wire (~625 MPa) as per the ANSI/NEMA WC 67 standard [33].

In cases where wire is drawn and still higher ductility is required (or drawing required for reduced roughness), select Integran processes are also capable of producing "ultra-fine" grained or alternative multi-layered

materials (e.g., NiCo alloys, Table 9). In this case, it is possible that a hybrid wire can be manufactured which can be drawn and which possesses properties approaching the CS-95® "soft temper" wire. It is also possible that such a wire will possess strength exceeding some other environmentally-hazardous cadmium-containing wire products, e.g., IWG-HPC's Tensile-Flex® 135 (UNS C18135) which possesses a typical strength of 500 MPa (73 ksi). The latter comparison is particularly important for military and aerospace applications as it is produced in much larger supply than CuBe wire: for example, IWG-HPC manufactures approximately 30,000 lbs per month of their Tensile-Flex® 135 wire (an order of magnitude larger than the CS-95® wire) *and in a range of gauge sizes* [32]. The electrical conductivity of the "ultra-fine" grained NiCo alloy (similar to nano NiCo, 13.8% IACS, Table 7) could also allow such a hybrid wire to approach the conductivity of the Tensile-Flex® product (90% IACS minimum).

8.0 SUMMARY

The focus of this two-Phase project was to develop a nanostructured metal material and process suitable for CuBe-replacement, then demonstrate this material and process in three CuBe product forms: bulk, sheet, and wire.

In Phase I, a number of processes were evaluated, and the material properties were compared to those of CuBe. In specific, methods to analyze grain size, surface roughness, microhardness, abrasive wear, sliding wear, and ductility, among others, were used to evaluate the performance of nanostructured materials (produced using Integran's pulse plating technology) against CuBe. Following this comparison, it was determined that – similar to current CuBe alternatives commercially available or in development elsewhere – select materials and processes may be able to serve as primary CuBe replacements in specific applications, e.g., bushings, rather than a unified CuBe replacement across all product platforms. As a result, Phase I was able to down-select four microstructurally-designed nanostructured metal-based materials which hold the most promise: nanostructured copper, nanostructured copper-nickel alloy, nanostructured nickel-cobalt alloy, and nanostructured cobalt alloy.

Phase I demonstrated that these nanostructured materials can be manufactured in forms applicable to the replacement of CuBe in products: near-net-shape sub-scale bushings were successfully manufactured for MIL specification bushing testing (to be performed in Phase II); Nanometal/composite hybrid sheets were fabricated which possessed superior weight-specific three-point bending performance relative to CuBe sheet; Nanometal thin films and thin film shapes were fabricated to demonstrate the process precision and flexibility relative to CuBe foil; and Nanometal-enabled conductor wire was produced in batches larger than 500' with a high level of process consistency and performance.

Phase II work continued the progress made in Phase I, focusing on four down-selected nanostructured platforms. It was observed that while some nanostructured platforms performed well compared to CuBe, some also had limitations. Of all the materials tested, nanostructured cobalt alloy possessed the most promising combination of galling resistance, low friction coefficient, hardness, strength, and performance as a bushing. *In fact, it was shown that the nanostructured cobalt alloy possessed perhaps the best performance of any currently-available CuBe-alternative bushing materials.* However this material had limited electrical conductivity, it was sensitive to coating defects, and it was ferromagnetic. Nanostructured nickel-cobalt could be engineered to possess encouraging results as a bushing. This alloy also possessed excellent results in bending fatigue on its own; it could be applied to carbon fiber substrate, which also possessed excellent

bending fatigue performance. This lends itself as a promising replacement to CuBe in sheet form. Nanostructured copper was limited in hardness and strength but has promise as an electrical conductor with galling resistance. Nanostructured copper nickel may be engineered to possess improved galling resistance, but its high thermal stability (marked by a stable electrical conductivity as a function of temperature) may offer its use in applications outside the range of CuBe.

Future work can target specific applications. For example, CuBe bushing alternatives can be targeted with the nanostructured cobalt alloy. This is the focus of a future effort and proposal with the Environmental Security Technology Certification Program (ESTCP) among other efforts. For example, bushing/bearing properties are primarily 'surface-constrained'. This leads to the possibility of applying the nano-material as a coating to an alternative substrate material (rather than machining the component from bar or rod stock). This could lead to lighter weight, as well as lower cost aerospace components. Integran is uniquely positioned to execute on such a development using its nanostructured metal technology as well as the application of that technology to light-weight substrates.

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