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## Friction stir processing / welding of NiAI bronzes

McNelley, Terry

Naval Postgraduate School, Monterey, California

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## New Materials and Methods

## Friction stir processing / welding of NiAl bronzes

#### Terry McNelley, Sarath Menon

#### Overview:

Friction stir processing (FSP) of as-cast NiAl bronzes converts the as-cast microstructure to a wrought condition in the volume of materials subjected to the process. This results in improved properties in the absence of component shape change. With the development of portable systems, friction stir processing may enable in situ repair of defective components such as propellers and thus avoid expensive procedures such as dry docking for such repairs.

#### **Project Description:**

Microstructure – mechanical property relationships associated with multi-pass FSP are now of primary interest in work on the cast NiAl bronze materials and have also been examined in Al alloys [8,9]. Factors that adversely affect ductility, especially in orientations transverse to the local direction of tool advance, have been identified. Recent results demonstrate that FSP tools and processing conditions must lead to high and uniform temperatures and strains in order to attain high ductility throughout the stir zone volume.

Applications of FSW in joining of similar and dissimilar metals are now growing rapidly. This process and FSP share many attributes although FSP is less well developed because it is a newer concept. Nevertheless, FSP will also experience rapid growth as the benefits of this unique metallurgical tool become fully apparent. Thus far, development of FSP/W has been largely empirical. The goal of sustained growth in utilization will depend significantly on improved understanding of the fundamental science involved in these technologies. This will also strengthen the underlying foundation in the development of standards for implementation in industry. Both applied and fundamental research activities in support of this goal are needed. Efforts in support of the transition of FSP technology to NiAl bronze propeller materials will be described first, followed by activities that will exploit new NPS capabilities. Finally, an approach to broader, fundamental problems of microstructure control during FSP/W will be outlined.

The thermomechanical cycle of the initial FSP pass on cast NiAl bronze induces characteristic phase transformations that are accompanied by distortion of the resulting microstructure constituents (i.e., the ? and ? phases). This is often reflected in the development of distinct, elongated primary ? and ? transformation products in as-processed microstructures. Recent studies involving Gleeble thermomechanical simulations as well as isothermal hot rolling have shown that local von Mises strains varying from 0 to ~3.0 may also be estimated from such distortions of stir zone microstructure constituents. Preliminary comparisons to typical stir zone microstructures suggest that one-third or more of a typical stir volume has experienced local equivalent strains ?3.0. In contrast, modeling has indicated that equivalent strains are >10.

FSP inherently involves multiple, overlapping passes and the step-over distance between successive passes is an important parameter in addition to the tool rpm/ipm combination. Uniform, equiaxed and refined microstructures, and the absence of texture within stir zones were produced by FSP with small step over distances and a step-spiral tool. Thus, multi-pass FSP results in recrystallization and grain refinement, homogenization, and redistribution of both the primary ? and ? transformation products. In contrast, excessive step over distance results in regions of less deformed stir zone material that, in turn, lead to strain localization and low apparent ductility.

## Research

New Materials and Methods

Mechanics of Materials

Materials Joining

Laser and Material Interaction

Energy Harvesting and Storage

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For more information, contact Terry McNelley at tmcnelley@nps.edu

## Underwater Crack Repairs in HY80 Structural Steel by Friction Stir Welding (FSW)

#### Terry McNelley, Sarath Menon

#### Overview

This program will determine the feasibility of performing crack repair on submarine control surfaces by underwater FSW of HY-80 steel. Microstructures and microstructure – mechanical property relationships will be established for the HY-80 material after FSW.

#### **Project Description**

Submarines exhibit fatigue cracking in the alloy steel (HY-80) plating on the control surfaces due to cyclic stresses caused by depth changes over the life of the ship. Fusion welding is not a practical method of underwater repair of these cracks. High cooling rates will promote the formation of the brittle martensite phase in the weld metal and heat affected zone, resulting in reduced toughness and increased susceptibility to hydrogen assisted cracking. The latter problem will be particularly acute because the welding arc will liberate hydrogen from the water, thereby facilitating hydrogen assisted cracking of the steel when this hydrogen is absorbed into the weld metal and surrounding heat affected zone. For these reasons the method currently available to the navy to repair these cracks is to dry dock the ship.

Control surface inspections and crack repairs are typically scheduled inside CNO docking availabilities, but because of the nature of the work these repairs can cause increased risk to the dry docking schedule and result in increased costs for the availability by delaying the undocking of the submarine. In order to repair cracks on the underside of the control surfaces, trapped water must first be drained or it can affect the quality of the weld repair. In order to drain the trapped water, holes often have to be drilled in the plating and the draining process can take days or even weeks to complete. A delay in undocking of a submarine can result in an increase in cost of \$100K per day just in support services alone. Due to tide restrictions on some of the Navy's drydocks, delaying the undocking by a single day may require shifting the undocking date by 2-3 weeks, with a resulting increase in cost on the order of \$1M. Additionally, the holes that were drilled need to be plug welded and often become starting points for future cracks.

Alloy steel (4142; 0.43% Carbon) plates (0.25 in thick) were successfully processed by Advanced Metal Products, Provo, UT using a proprietary tool composed of cubic boron nitride (CBN) particles dispersed in a W-Re alloy matrix. One plate was processed dry and the other was immersed in a water tank to a depth of approximately 4 inches. Cooling was supplied to the water box via copper tubing containing refrigerant from the FSW machine. Photos taken during the FSP operation under both dry and wet conditions are presented in Figure 1 to illustrate the underwater setup and also to compare the steel sample behavior under these conditions.



Figure 1. Photographs showing the FSP runs in dry (left) and wet conditions (right). Notice the obvious temperature difference at the tool surface during these runs and the formation of steam bubbles.

Several RPM/IPM combinations were performed in order to establish a successful processing parameter window where defect-free welds could be produced underwater. Based on the observations here a combination of 400rpm/2ipm was found to be sufficient to produce

defect free runs both during dry and wet runs. The progressions in the microstructural development during the dry and wet runs were followed by examining the details of the microstructural constituents and are summarized in Figure 2.



Figure 2: The base metal exhibits a ferritic – pearlitic microstructure in (a), consistent with a normalized 0.43wt. pct. C alloy steel. FSW at 400 rpm and 2 ipm results in a microstructure constituted of fine martensite consistent with local peak temperatures well above 800°C.

Figure 2(a) illustrates the ferrite + pearlite microstructure in the as- received 4142 steel plate and Figures 2(b) and (c) illustrate the martensitic microstructure observed within the stir zone of the dry and wet runs, respectively. The microstructural constituents in both the cases were quite similar though the thermomechanically affected zone (TMAZ; comparable to the heat affected zone in conventional fusion welding) was much wider in the dry run in comparison to the wet run. It appeared that the pearlitic constituents were always absent within the stir zone suggesting that the austenitization was completed within the stir zone in both the dry as well as the wet FSP conditions. Martensitic microstructure was observed within the SZ and appeared quite uniform throughout this region in all samples

For more information, contact Terry McNelley at tmcnelley@nps.edu

# Multi-Material Dielectrics: Super High Dielectric Constant Materials

#### Jonathan Phillips

#### Overview:

Develop novel multi-material dielectrics (e.g. Table, Samples 4-10) with dielectric constants far better than standard (Table, Sample 3) to create capacitors of unprecedented energy density. Initial results show that below 3 volts we have achieved higher energy density than that found in commercial electrolytics. Example: Figure shows MMD producing equivalent to a 10,000 ?F capacitor in far less volume than a commercial equivalent.

#### Project description:

The primary goal of this research is to create novel metal based dielectric material(s) (MMD) with dielectric constants far greater than those of any previous material such that electrostatic and electrolytic capacitors of unprecedented energy density can be created. A second goal of the work is to develop a model of the dielectric constants of the MMD.

These materials consist of metal coated with aninsulating layer, in a variety of geometries. The underlying paradigm to this design is simple. The metal in the MMD provides a near infinite permittivity and the insulating layer around each metal element prevents discharge, by preventing percolation, between electrodes. In theory and practice materials with the highest permittivity yield the highest dielectric constant. Hence, the energy storage component in the MMD is in a phase (metallic) with the highest permittivity. Yet unlike simple metal, this metal is coated with an insulating layer, preventing a short, even by percolation at low loading, between electrodes. The net is a composite material with super high dielectric and a high resistance. Serendipity in earlier work supports this postulate.

Remarkable initial results justify the proposed effort. We documented, confirmed by independent lab, the existence of a new family of dielectric materials, with measured dielectric constants between 10 and 10000 times those reported for barium titanate, the standard high performance material generally employed in electrostatic capacitors (Table I).

In order to test these materials 'electrolytic configuration' was adopted and the RC time constant directly measured. A standard configuration was used: 5 cm diameter x 0.4 + / -0.1

cm thick 'pucks' consisting of MMD material encapsulated in wax were placed between aluminum electrodes, also 2.5 cm diameter, in a simple hard plastic rig. In order to prevent any leakage, a very thin layer of electrolyte was placed between the MMD puck and one electrode.

In Figure 1 the results made using silica coated (decomposed TEOS) 5 micron Ni particles as the MMD are presented. An equivalent dielectric constant of >109 at 1.5 V, a value consistent with those measured with the meter, was measured. Results of this nature were obtained with a number of remarkably inexpensive and ordinary conductive materials serving as the conductive phase of the MMD, including silica coated (decomposed TEOS) commercial carbons supplied by Cabot, Corp. For example, one carbon based (Vulcan X-72) MMD puck yielded a capacitance of 0.5 F at 50 mV, or an equivalent dielectric constant of >1011. Results are consistent with hypothesis that conductor identity is of tertiary significance.





Tremendous effort is underway to generate novel energy storage materials, particularly supercapacitors and battery/supercapacitor hybrids. Supercapacitors appear fundamentally limited because the design will not hold charge to a high voltage, clearly limiting energy density. 'Hybrid' battery/capacitors have far higher energy densities than standard capacitors, and discharge more quickly, delivering power better than batteries, but still fall short for both energy density and power delivery. The new 'energy storage' modality we are proposing to study is fundamentally different than any of the other new devices. The principle difference can be simply distilled: Unlike other new modalities, in the method we are proposing, there is no electrolyte, no ionic current. Another difference is there is no need for exotic morphologies such as high surface area electrodes, complex nano-scale coating technologies, nanoparticles or expensive metals (e.g. Ru). We believe we have simply invented a new class of dielectrics, such that in capacitor architecture, only electrons are mobile. And the best results are also easily summarized: At low voltages (ca.<3 V) the energy density (volume basis) of electrolytic style capacitors made with MMD is several times greater than that available from commercial electrolytic capacitors, the style of capacitor generally employed for energy storage.

The primary objective of the first phase of work will be empirically driven effort to understand the connections between production variables and dielectric behavior. We will employ statistical software (JMP) to create simple algebraic correlations between performance and production variables that will include metal identity, method for creating insulating layer on metal particle, insulating layer thickness, metal particle size, net particle loading, matrix material (particularly conductivity of matrix material), puck thickness. In addition to the simple measurement technologies presently being employed (e.g. direct measures of the RC time constant as a function of voltage), other measurements will be made to assess frequency response, maximum effective voltage, power delivery. All required measurement technology, as well as all production capacity, is readily available at NPS. Another aspect of the work will be to test these MMD in a variety of configurations such as simple electrolytic capacitor, and a variety of the new 'hybrid' designs.

For more information, contact Jonathan Phillips at jphillip@nps.edu

## Realization of Micro-Ion Thrusters through Carbon Nanotube Field Ionization Engines

Sebastian Osswald1,2, Dragoslav Grbovic1, Oscar Biblarz2, Marcello Romano2, Darrell Niemann3

1Department of Physics, Naval Postgraduate School, Monterey, CA

#### 2Department of Mechanical and Aerospace Engineering, Naval Postgraduate School, Monterey, CA 3NASA Ames Research Center

#### Overview:

We propose the development of a miniaturizable ion engine by exploiting the field ionization of a propellant gas through the use of arrays of carbon nanotubes (CNT). The new field ionization engine technology could reduce the volume of ion thrusters by 80-90 % compared to currently employed electron-bombardment designs and enable the development of very small satellites and spacecraft.

#### **Project Description:**

We are developing a novel carbon nanotube field ionization engine (CNT-FIE) that will, for the first time, allow for the design of scalable micro-ion thrusters. The unavailability of miniature ion thrusters is the solely remaining factor that inhibits the implementation of novel pico- and nanosatellite technologies.

Ion thrusters have been used successfully in several unique space missions to provide continuous thrust with a high specific impulse for very long times (~years). This characteristic and their high efficiency make ion thrusters the perfect choice for earth-orbit stabilization of satellites and for in-space propulsion of spacecraft. Furthermore, due to the small amounts of propellant required during operation, ion thrusters are ideal candidates for use on small spacecraft (including micro-, nano- and pico-satellites).

The original cesium-contact ionization thruster (though scalable and efficient), developed in the 1960's, was found to be impractical for space use due to the toxicity of cesium and the metallic character of the propellant. Its replacement, the current state-of-the-art ion thrusters, such as DC electron-bombardment and RF ion sources are large, massive, and difficult to downscale because of the magnetic fields and/or the size of chamber size.

Using field ionization of a propellant gas by of arrays of carbon nanotubes (CNT) allows us to significantly decrease the size of the ionization chamber and design a miniaturizable ion engine. The field ionization-based ion engine technology could reduce the volume of ion thrusters by 80-90 % compared to currently employed electron-bombardment designs. The new ionization technology will also enable significant mass and power savings to ion thrusters of any scale, and will allow for revolutionary new missions that utilize very small spacecrafts.

For more information, contact Sebastian Osswald at sosswald@nps.edu

### Nanocarbon-reinforced metal armors

#### Sebastian Osswald, Luke Brewer, Joseph Hooper

#### **Project Description**

The goal of this project is to develop lightweight metal composites that are reinforced against blast and projectile impact by nanocarbon inclusions. Carbon nanomaterials, such as carbon nanotubes (CNTs), the strongest and stiffest material yet discovered, or nanodiamond (ND), the hardest material found in nature, can be embedded in a metal matrix to form a composite with significantly improved mechanical and tribological properties. These offer greatly enhanced armoring as compared to traditional composites, such as those using micron-sized carbon fiber reinforcement. The stress imparted on the metal matrix is transferred in large part to the significantly stronger nanotubes via their interfacial bond with the metal. The proposed composites also improve on many other desirable properties of the bare metals, including enhanced electrical and thermal conductivity and improved resistance to friction and wear.

The greatly increased hardness and tensile/yield strengths of nanocarbon-metal composites (NMC) are expected to provide improved resistance to blast and fragment impact. Much like the case of ceramic armors, such as boron carbide, high material hardness improves resistance to plastic deformation for lower velocity impacts, and aids in fracturing the projectile on impact at high velocities. In addition to the enhancement provided by CNT reinforcement, we plan to pursue synthesis efforts that disperse additional nanodiamond (ND) throughout the CNT/metal matrix, leading to a novel type of NMC that contains two different carbon nanomaterials.



The composite synthesis will follow two different approaches that are based on a layered composite design (Figure 1a) and an integrated composite design (Figure 1b). The layered design consists of an aluminum/ND layer that is sandwiched between two aluminum/CNT composite layers which provide high hardness and high toughness, respectively. By varying the thicknesses of the AI-CNT layers we can control the ratio between the hardness and the toughness of the composite casing. The integrated design concept is based on a hybrid nanocomposite that includes both highly dispersed CNT and ND additives in a single layer material. In this case, hardness and toughness can be controlled by adjusting the concentration of the ND and CNT additives, respectively.

For more information, contact Sebastian Osswald at sosswald@nps.edu

## Organometallic clusters as novel energetic materials

#### Joe Hooper, Jim Lightstone, Chad Stoltz

#### Overview:

The goal of this work is to explore molecular scale aluminum clusters that are stabilized against oxidation by direct bonds with organic ligand groups. These small clusters crystallize into low-symmetry solid-state structures, and may offer a route to extremely rapid combustion of aluminum that is quite unlike the standard diffusion limited burning of metal particles. This would provide several advantages for solid rocket motor and energetic materials.

#### **Project Description:**

The addition of metallic fuels to advanced energetics is now a standard way to increase the overall energy density of warheads. Micron or smaller powders of aluminum result in significant increases in the volumetric heat of combustion of a charge, but the timescales on which aluminum can combust are limited by well-known diffusion and kinetic processes. In this project we are considering a new class of materials that combine the favorable energy density of metallic fuels with the fast reaction rates more characteristic of explosives and propellants.

Our initial work has examined a range of aluminum organometallic clusters that were previously synthesized by Schnöckel and coworkers at the University of Karlsruhe. An example material is given in the above figure; this consists of a 50 atom aluminum core, surrounded by 12 organic ligands bound covalently to surface aluminum atoms (shown in teal). This general form, with a metallic core bound to surrounding organic ligands, is the basic motif for materials we are studying. Small crystallized quantities of a few aluminum organometallic clusters were studied in Germany by 27AI NMR and x-ray diffraction in inert cells, but virtually nothing is

known about their thermal stability, decomposition pathways, reactivity to air, and so on. We have performed density functional theory and quantum molecular dynamics simulations of these materials, which have demonstrated that they may have favorable energetic properties.



First, the energy density even of known, unoptimized materials is already very high. The calculated heat of combustion (in air) per unit volume is shown in the above figure for RDX, an aluminized HMX formulation (PBX), pure AI, and for the Al50Cp\*12 system displayed above. This organometallic cluster is already 60% the energy density of aluminum due to its very high enthalpy of formation (~1800 kcal/mol), strained aluminum core, and surrounding hydrogenrich ligands. Our calculations also suggest that the combustion rates are potentially much higher than diffusion limited Al burning, as would be expected. An analysis of the bond strengths of the systems, combined with constant-temperature quantum molecular dynamics simulations, all suggest that the initial decomposition step is likely the loss of surface AlCp\* units. The zero-temperature barrier for this is approximately 50 kcal/mol, and removal of these surface groups would expose a highly reactive, completely unoxidized aluminum core.

Aluminum organometallic complexes offer a number of significant benefits for DoD applications, if they can be made air and temperature sensitive. Their high energy density and fast energy release would allow for reductions in warhead size. The potentially high burn rates and high volumetric heats of combustion would allow for new solid rocket motor designs, such as a fast end-burner.

For more information, contact Joe Hooper at jphooper@nps,edu

