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COPPER-MULTIWALL CARBON NANOTUBES AND COPPER-DIAMOND COMPOSITES FOR ADVANCED ROCKET ENGINES

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Overview

- Introduction
- Research Team
- Analytical Modeling of Contact Conductance
- Experimental Procedure
  - Blending, Sintering
  - Thermal Property Measurements
  - Microstructure Analysis
  - Separation and Coating
- Results
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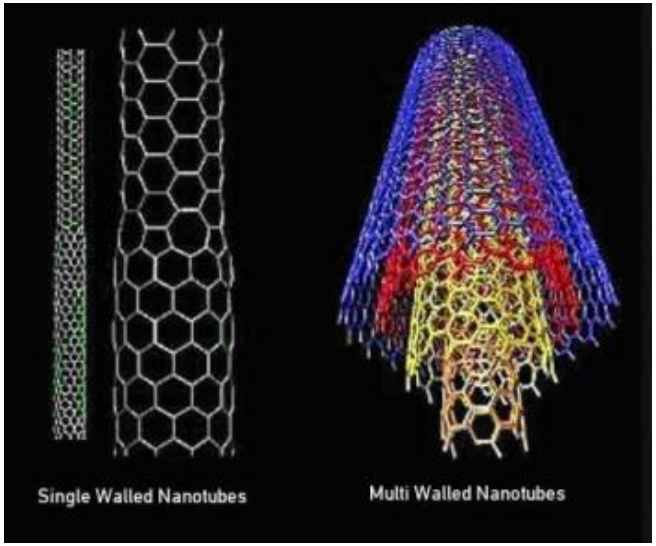
- Recommendations

Introduction

- Liquid-fueled rocket engine combustion chamber liners are regeneratively cooled and require high thermal conductivity material to maintain a low surface temperature.
- NARloy –Z (Cu-3wt%Ag-0.5%Zr alloy) is the state-of-the-art alloy used for liners.
- Single and Multiwall Carbon Nanotubes (SWCNT and MWCNT) are reported to have very high thermal conductivity, up to 10X that of NARloy-Z.



Research goal:
To improve the thermal conductivity of combustion chamber liner material NARloy-Z by 2X by embedding high thermal conductivity MWCNT in NARloy-Z matrix

Research Team

- Biliyar N. Bhat
  - NASA-MSFC, Principal Investigator
- David L. Ellis
  - NASA-GRC, Co-Investigator
- Vadim Smelyanskiy & Michael Foygel
  - NASA-ARC
- Jogender Singh and Aaron Rape
  - Applied Research Laboratory, Pennsylvania State University
- Yogesh Vohra & Vinoy Thomas
  - University of Alabama Birmingham
- Deyu Li and Kyle Otte
  - Vanderbilt University

Approach to Improving Thermal Conductivity Using MWCNT

- Significant effort has gone into thermal conductivity improvement using MWCNTs, but with limited success
- Problem: contact thermal resistance between MWCNT and matrix is high due to differences in thermal conductivity mechanisms
  - Copper: largely electronic conductor
  - MWCNT: conductivity by phonons (lattice vibrations)
  - Cu-MWCNT composites show lower thermal conductivity than copper
- Challenge: how to provide a low contact thermal resistance interface between Cu and MWCNT
- Approach: use carbide forming metallic elements (such as Cr, Ti, Zr) in the Cu-matrix to react with carbon in MWCNT to form a metal carbide
  - Metal carbides are believed to provide a higher contact conductance
  - Supported by literature in Copper-Diamond (Cu-D) system in which thermal conductivity improvements were reported by using Ti and Cr
- NARloy-Z was selected as matrix alloy
  - Logic: Zr in the NARloy-Z-matrix will react with MWCNT to form ZrC at the MWCNT interface
  - ZrC at MWCNT interface should improve contact conductance

Quantum Mechanics-Based Modeling of Contact Conductance (ARC)

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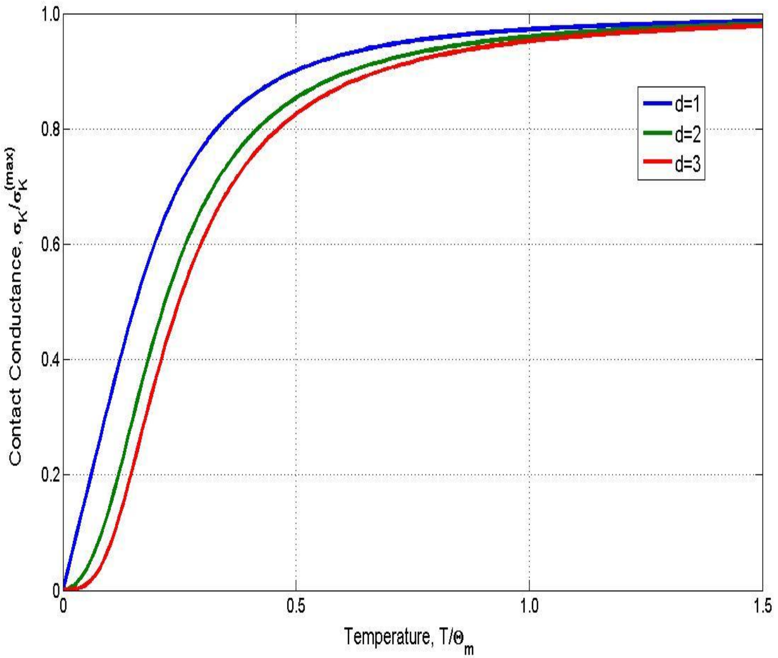


Parameter / Contact	Θ_m, K	σ^{max}, kW/cm^2K
D/Cu	310	6.6
D/Zr	250	3.5
D/Ag	221	2.4
D/ZrC	680	70
ZrC/Cu	310	35
D/ZrC/Cu	680, 310	23
CNT/Cu	310	$8.9\cdot10^{-13}$, *kW/K*
G/Cu	310	$2.6\cdot10^{-6}$, *kW/cm·K*

(Left) Contact Conductance of Metals with Carbon Modifications: d = 1 (*CNT*), d=2 (graphene, *G*), d = 3 (diamond, *D*). Here θ_m – temperature at maximum phonon frequency (kT = h x frequency where k is Boltzmann's constant and h is Planck's constant) – Debye's temperature is used for θ_m as an approximation. (Right) Contact thermal conductance for various interfaces

Observations:

- CNTs and diamond show similar contact conductance behavior at T/ θ_m >1
- D/ZrC/Cu contact conductance is significantly higher than direct CNT/Cu contact (by >3.5x)

Approach: Study NARloy-Z-MWCNT and NARloy-Z-D in parallel

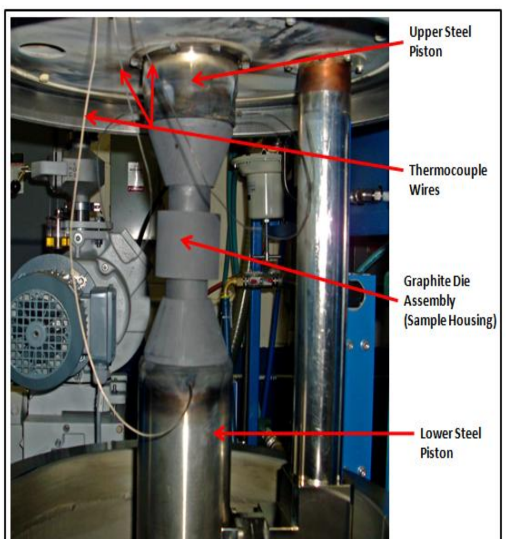
NARloy-Z-MWCNT and NARloy-Z-D Composites Studied

Material/Process	Vol.% (CNT/D)	Wt.% (CNT/D)	Density (gm/cc)	Characterization
NARloy-Z baseline (FAST)*	0	0	9.13	Thermal conductivity, mechanical, microstructure
NARloy-Z-MWCNT (FAST)*	1	0.25	9.06	Thermal conductivity
	2	0.5	8.99	Thermal diffusivity
	5	1.25	8.78	Thermal conductivity, mechanical, microstructure
	10	2.5	8.44	Thermal conductivity, mechanical, microstructure
	20	5	7.75	Thermal diffusivity, microstructure
	40	10	6.38	Microstructure
NARloy-Z-MWCNT (Extrusion)	1	0.25		Microstructure, electrical resistivity
	5	1.25		Microstructure, electrical resistivity
	10	2.5		Microstructure, electrical resistivity
NARloy-Z-Diamond (FAST)*	10	2.5	8.44	Thermal conductivity, microstructure
	20	5	7.75	Thermal conductivity, microstructure
	40	10	6.38	Thermal conductivity, microstructure
*Parameters used for FAST: Temperature: 975^{0}C, Pressure: 65 MPa, Heating rate: 10^{0}C, Holding time at temperature: 20 minutes, Furnace cooled				

Blending and Sintering of NARloy-Z-MWCNT

Attritor used for blending NARloy-Zand MWCNTs (GRC)

Left: Attritor in operation
Right: Attritor parts



Field Assisted Sintering Technology (FAST) (ARL – Penn State)

Left: FAST Apparatus
Right: Sintering at high temperature

Thermal Property Measurement

- Thermal diffusivities (α) of sintered NARloy-Z-MWCNT composites were measured by laser flash technique
  - Thermo-Physical Research Laboratory (TPRL) – Thermal diffusivity and thermal conductivity
  - NASA-MSFC -- Thermal diffusivity only
- Bulk density (ρ) was calculated from mass and geometry
- Specific heat (C_P) was measured using a differential scanning calorimetry
- Thermal conductivity (λ) was calculated using the equation

$$\lambda(T) = \alpha(T)\, C_P(T)\rho$$

MWCNT Thermal Conductivity Measurement

Thermal conductivities of MWCNTs used in this study (provided by Pyrograf, Inc.) and from other suppliers was measured at Vanderbilt University

Method used:

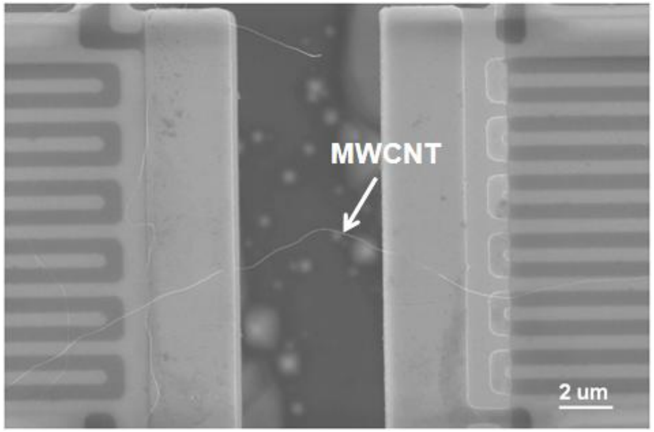
•Individual MWCNT sample was placed between two suspended membranes with integrated platinum coil serving as heat source and heat sink

• Platinum coil serves as both electric heater and resistance thermometer

• Dimension of sample was determined by electron microscopy

• Thermal conductivity of sample was calculated

• Contact resistance between sample and membrane is considered and sometimes eliminated by making measurements on two different lengths of the same sample



A MWCNT sample on the measurement device

Results: Ball Milling

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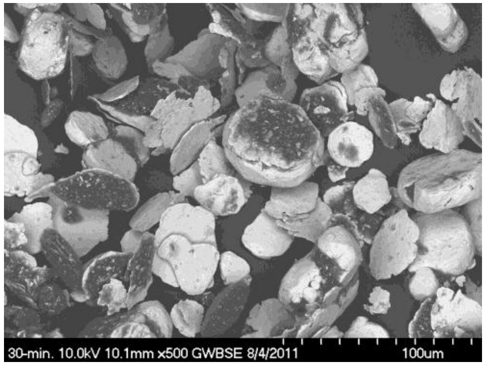
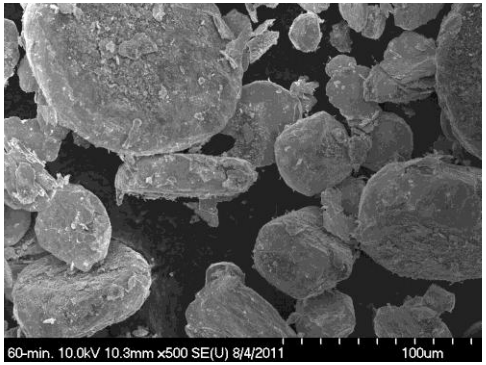
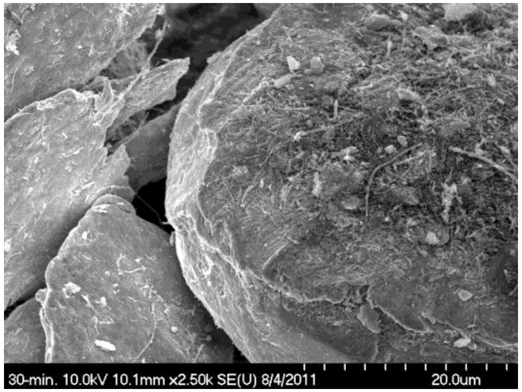


30 minutes

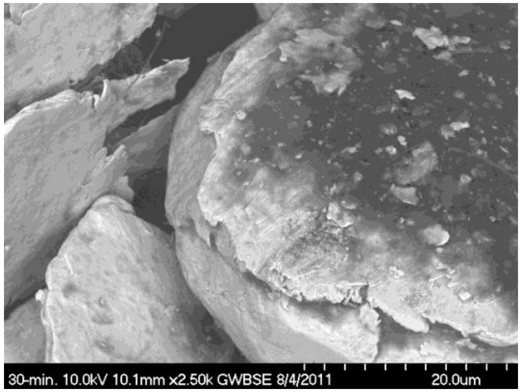


60 minutes

Powder morphology evolution during ball milling for NARloy-Z-10%MWCNT



Secondary Electron Image



Backscattered Electron Image

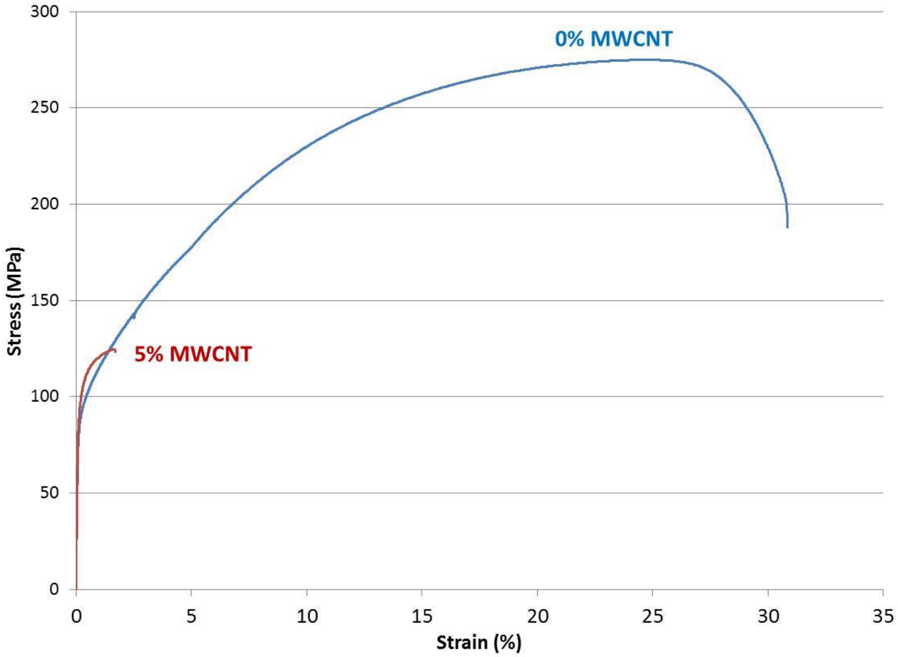
Typical NARloy-Z – MWCNT Composite Powder Particle Surfaces

Observations:

- NARloy-Z powder particles work hardened quickly during milling and started to grind after 60 minutes
- Blending time was limited to 45 minutes to prevent damage to MWCNT
- Portion of MWCNT was left on the powder particle surfaces
- **It was not possible to completely embed the MWCNTs in NARloy-Z**

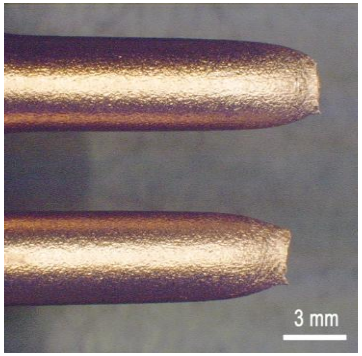
NARloy-Z-MWCNT Tensile Properties

% MWCNT	Average Yield (MPa)	Average UTS (MPa)	Average Elongation (%)	Average R.A. (%)
0	88.2	271.7	31.3	61.2
5	105.9	124.7	1.6	1.2
10	97.8	107.5	0.8	0.8

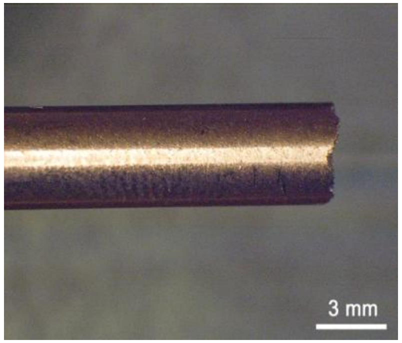


Stress-strain curves for baseline pure NARloy-Z (0% MWCNT) and NARloy-Z-5% MWCNT

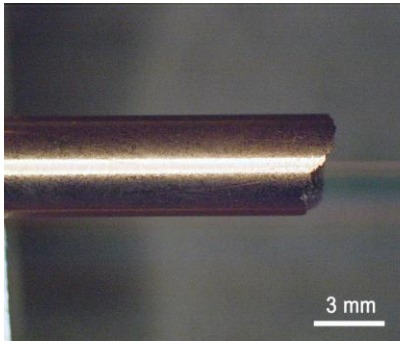
NARloy-Z-MWCNT Tensile Fracture Surfaces



0% MWCNT

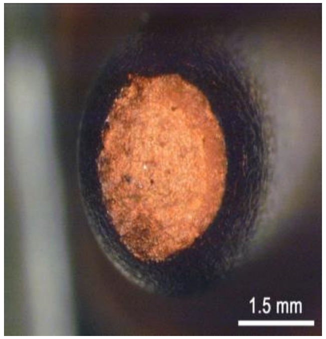


5% MWCNT

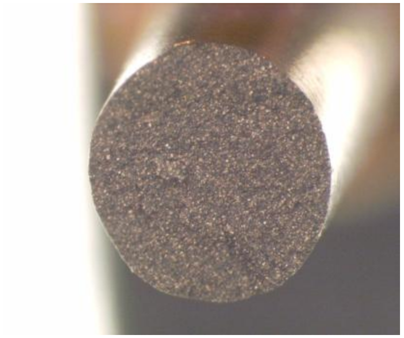


10% MWCT

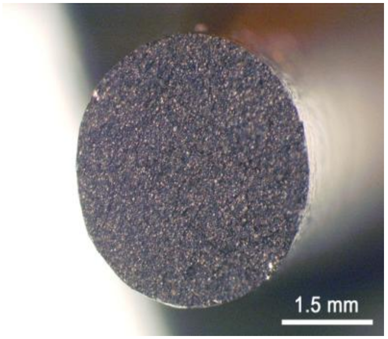
NARloy-Z-MWCNT tensile specimens



0%MWCNT



5% MWCNT



10% MWCNT

NARloy-Z-MWCNT tensile fracture surfaces

NARloy-Z-MWCNT Thermal Conductivity
(TPRL)

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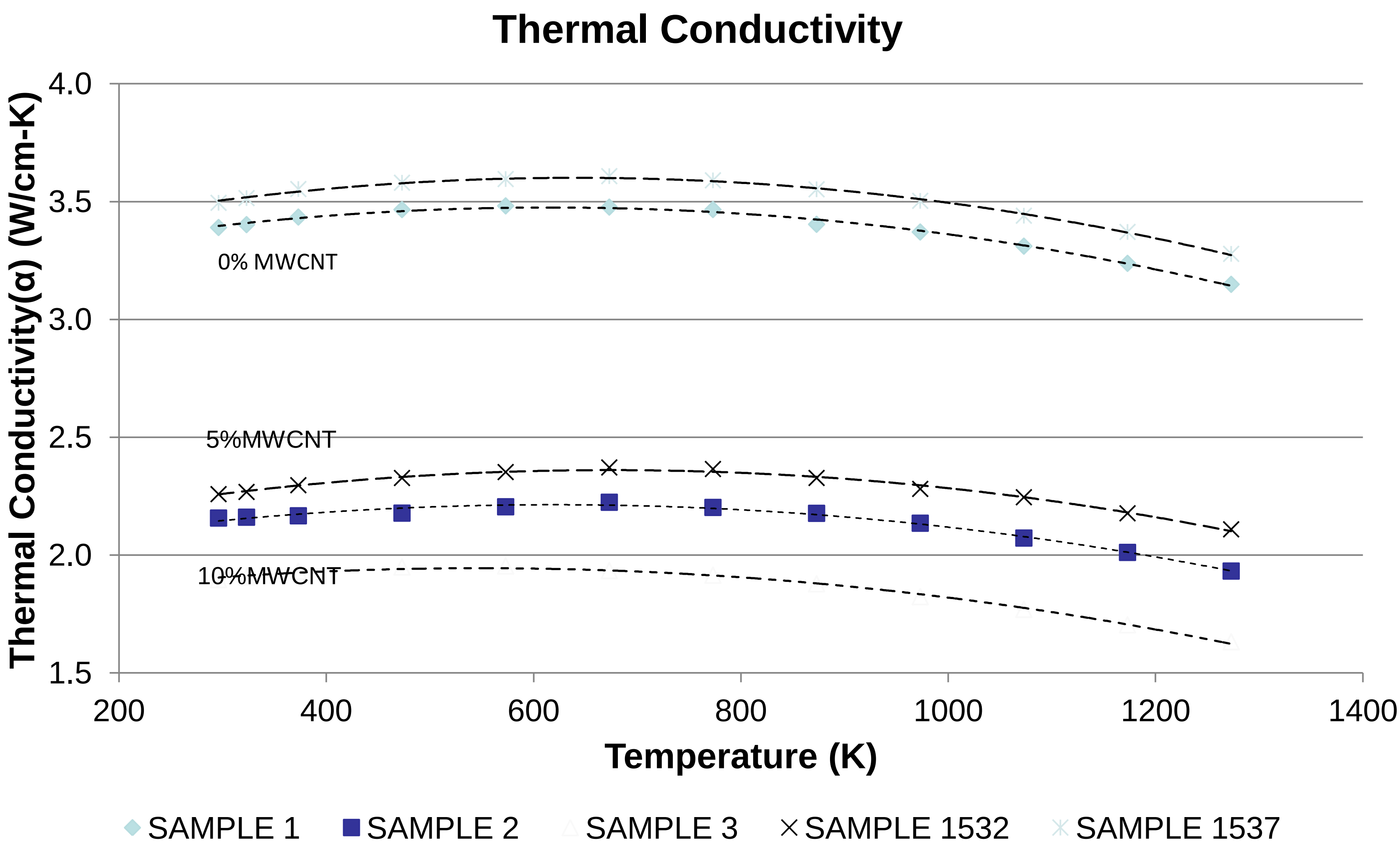

NARloy-Z-MWCNT Thermal Diffusivity
(TPRL)

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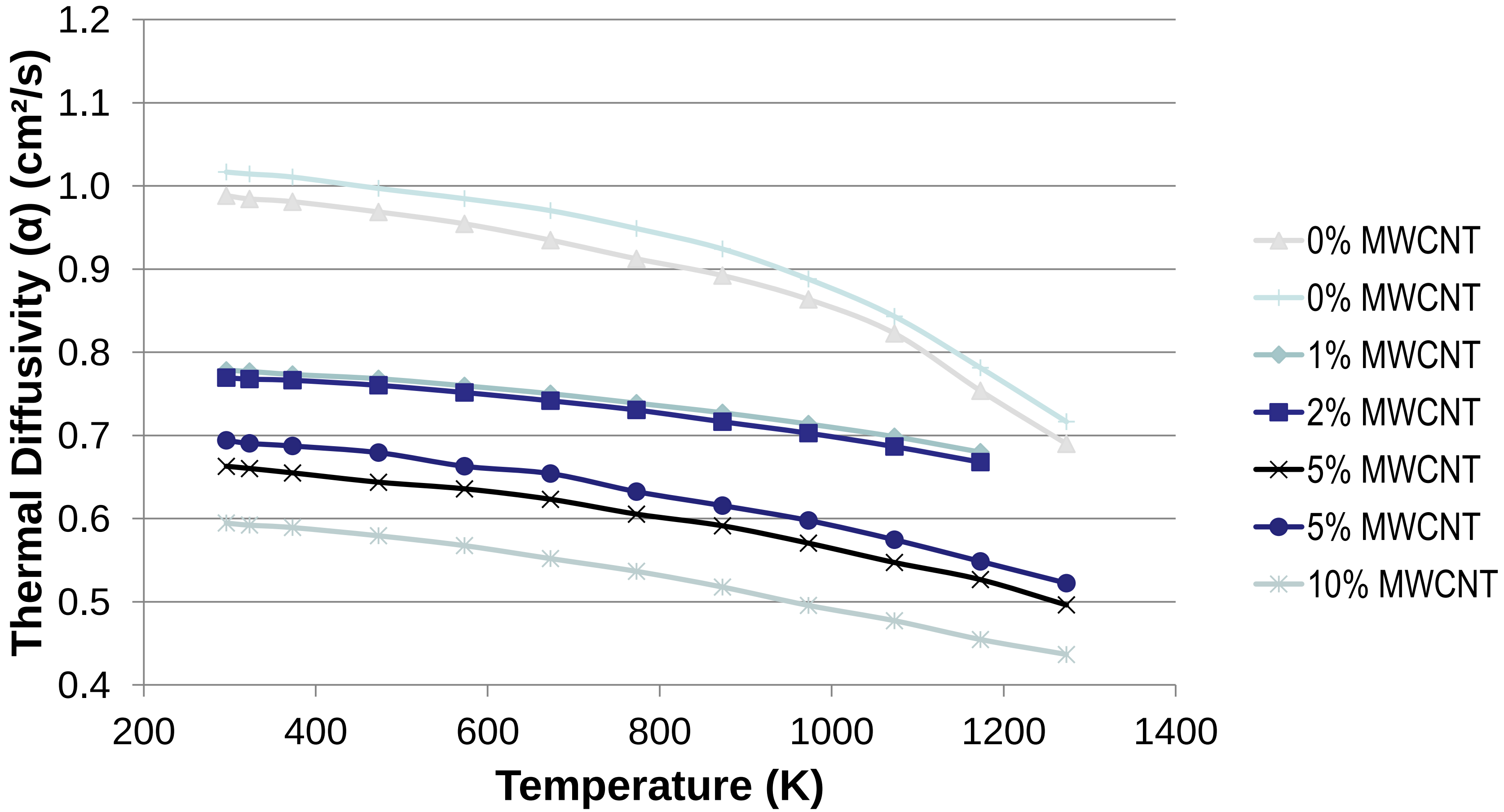

NARloy-Z-MWCNT Thermal Diffusivity
(MSFC)

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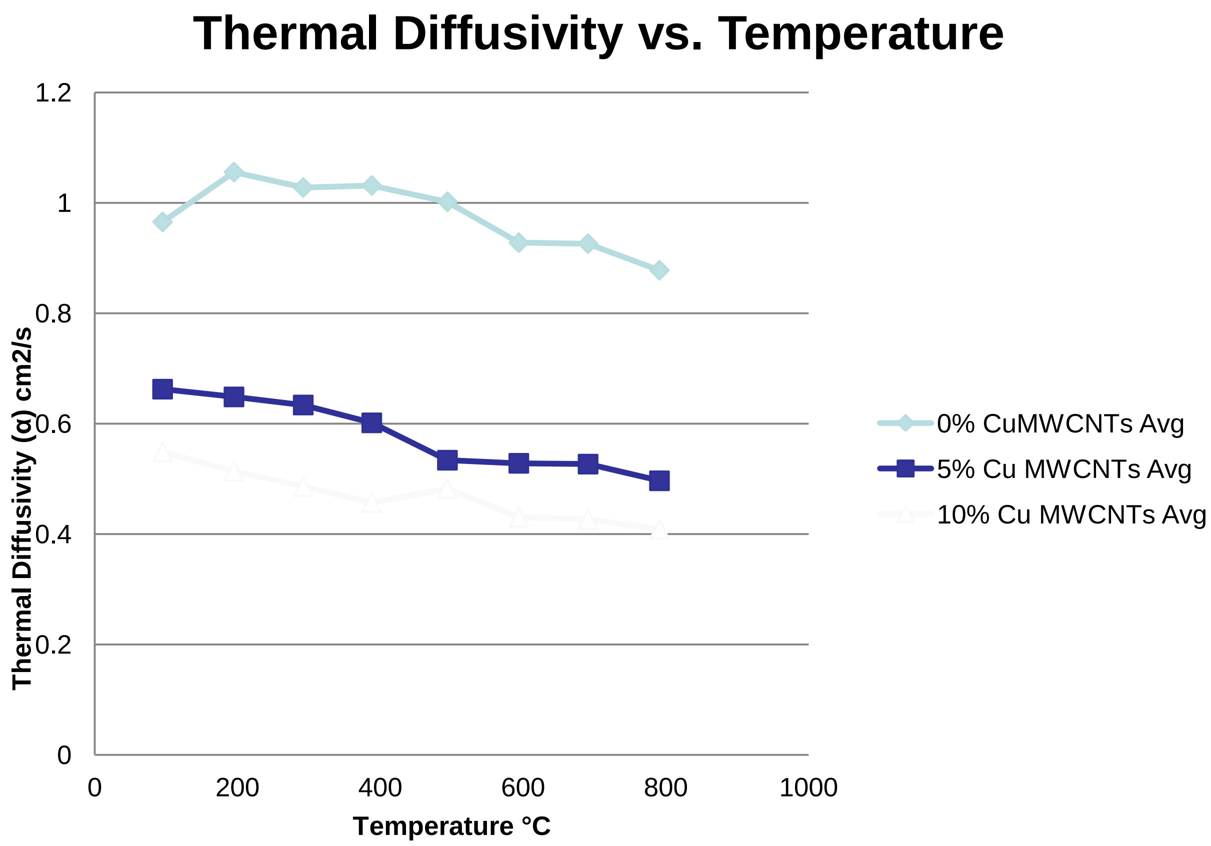

Thermal Conductivity of NARloy-Z-D Composites at Room Temperature (ARL)

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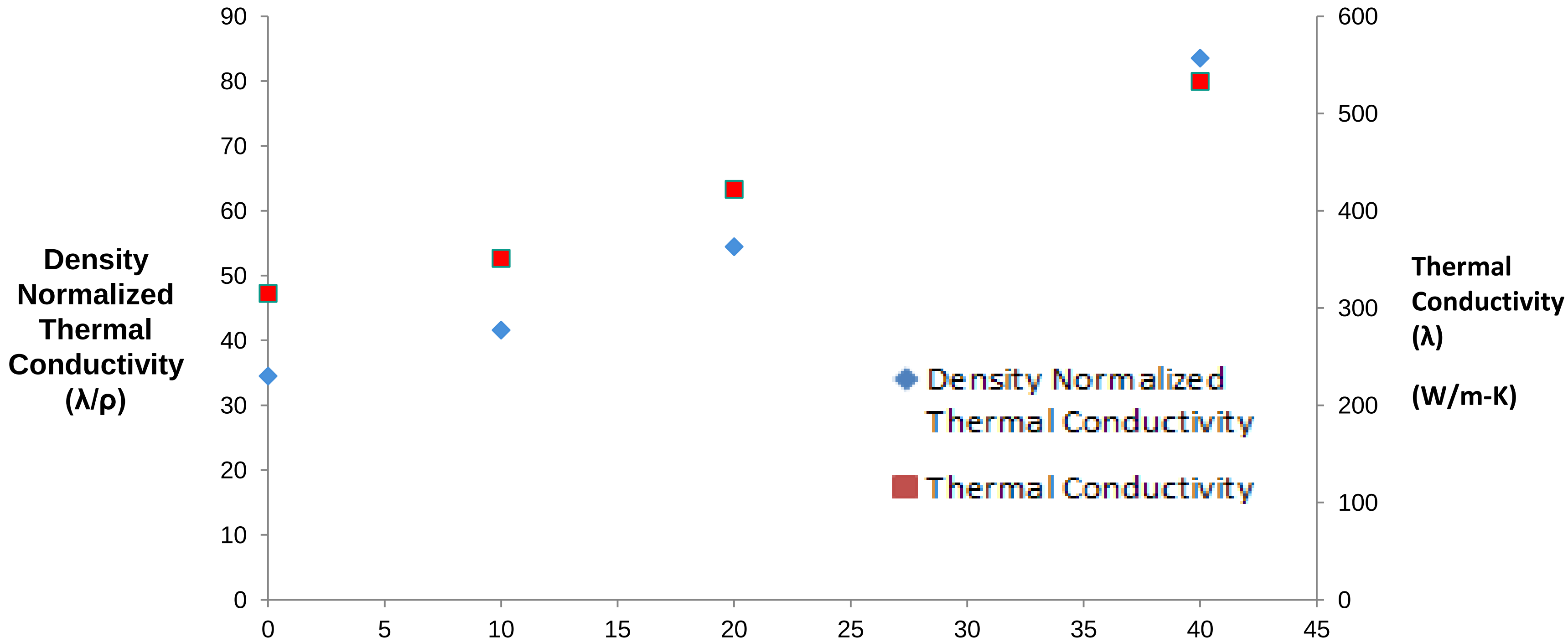
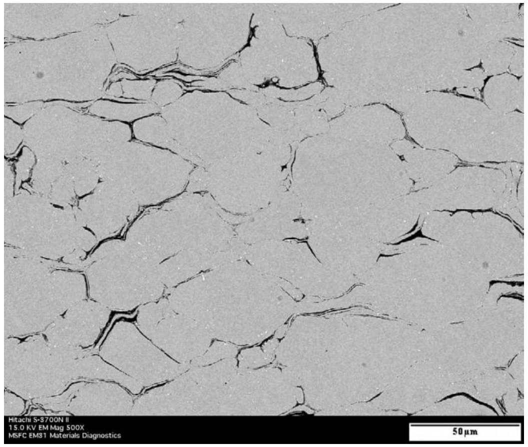
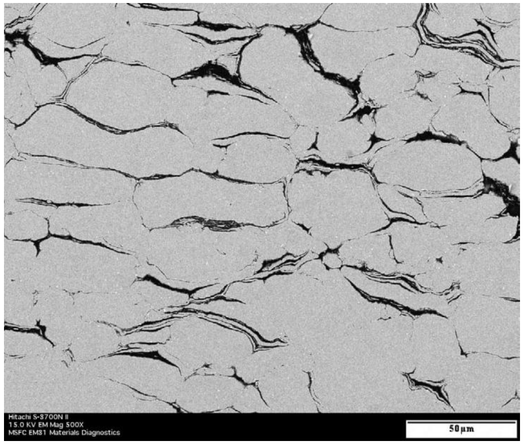


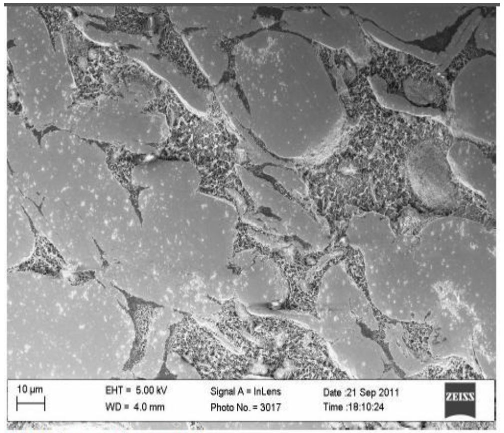
Sample	Vol. % Dia	Thermal Conductivity (λ), W/mK	Density, ρ (gm/cc)	λ/ρ
CuAgZr (NARloy-Z)	0	315	9.13	34.50164
CuAgZr+10 vol % D	10	351	8.44	41.58768
CuAgZr + 20 vol % D	20	422	7.75	54.45161
CuAgZr + 40 vol % D	40	533	6.38	83.54232

Microstructure Analysis

SEM images of NARloy-Z-CNT composites





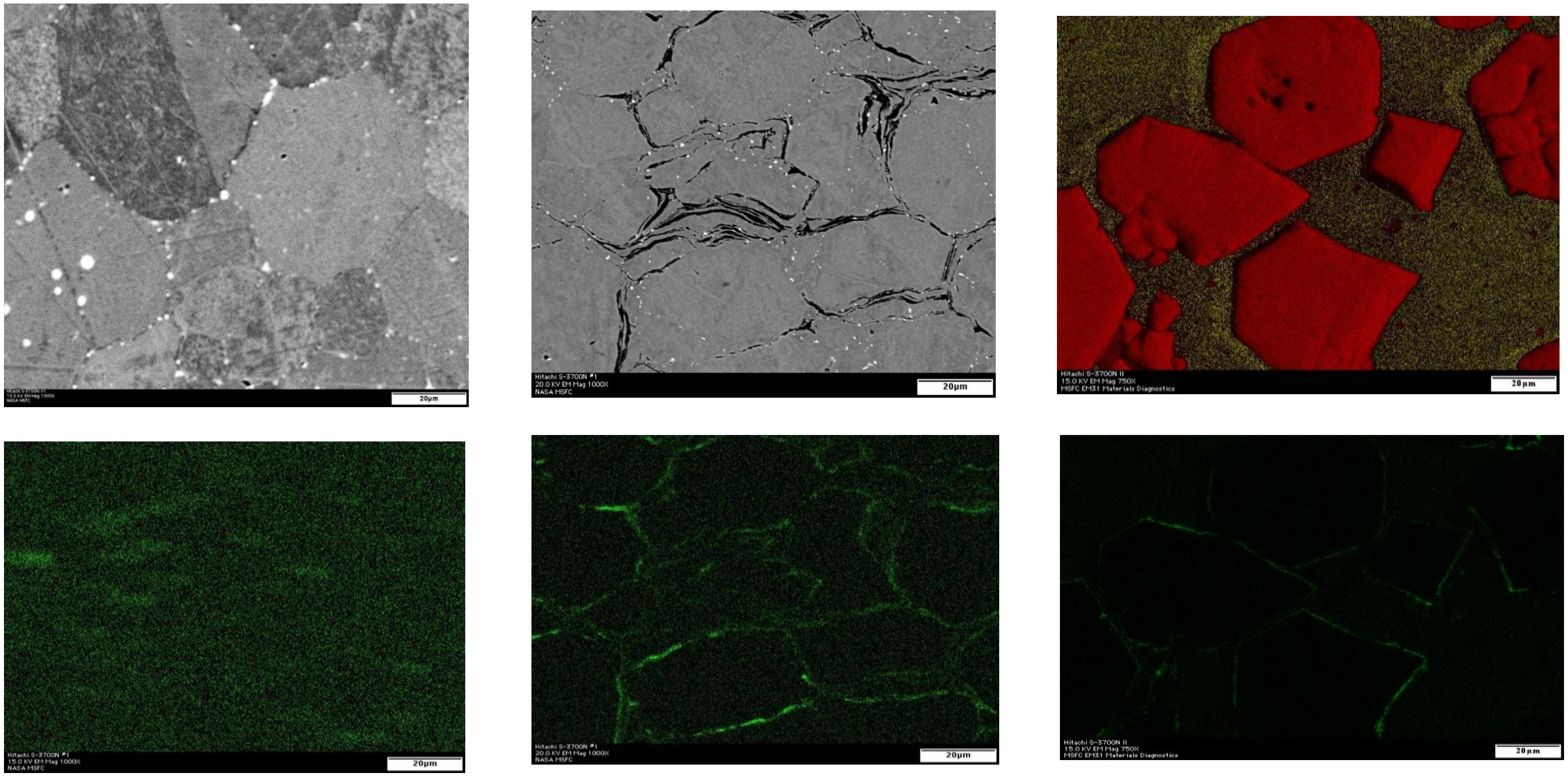


1544 NARloy + 20%vol CNT FESEM

NARloy-Z-5%MWCNT NARloy-Z-10%MWCNT NARloy-Z-20%MWCNT

Note the segregation of MWCNT at prior particle boundaries

SEM – EDS Analysis

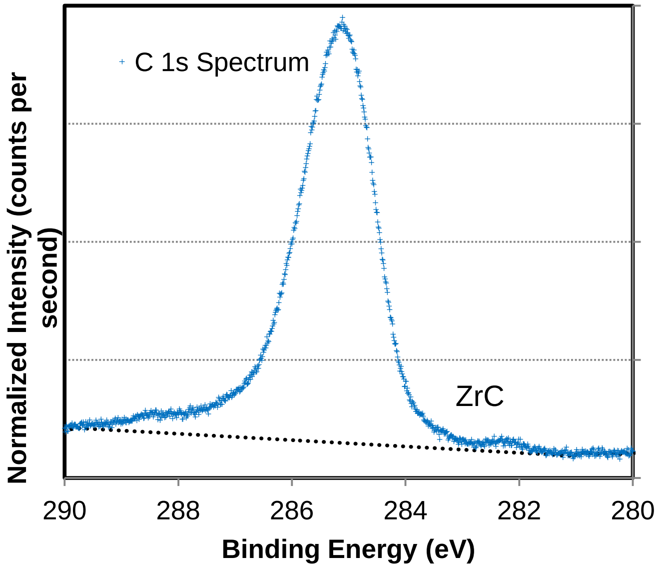


Narloy-Z- 0% MWCNT NARloy-Z-2%MWCNT NARloy-Z-20%D

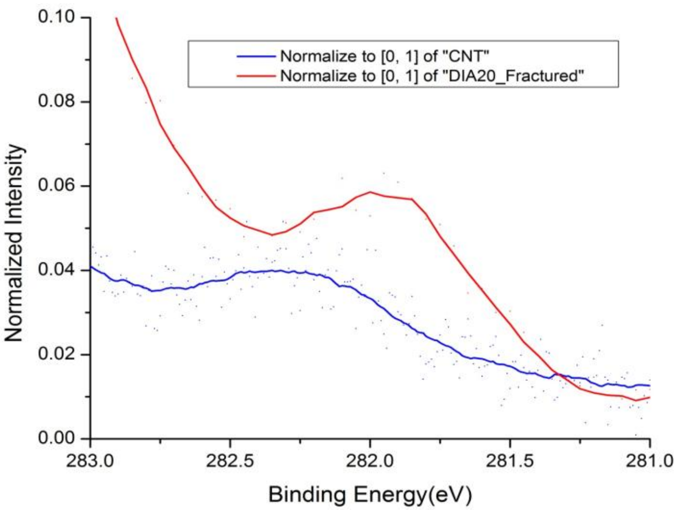
NARloy-Z –MWCNT and NARloy-Z-D composite showing Zr elemental map

Note the migration of Zr to MWCNT and D

XPS Analysis



XPS C 1s spectrum showing a small ZrC peak for a 1% MWCNT-NARloy-Z interface

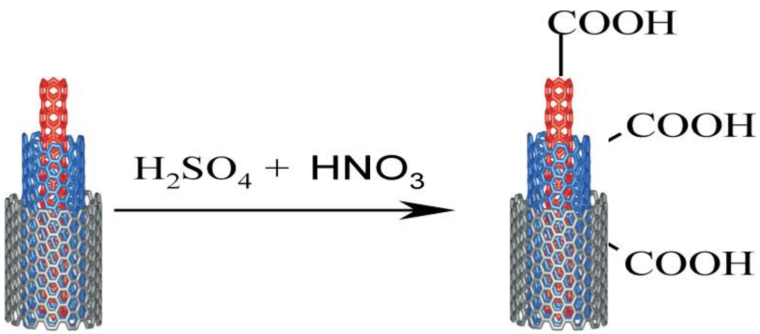


XPS Analysis of NARloy-Z-1%MWCNT and NARloy-Z-20%D composites showing ZrC peaks.

Note: Peak height for ZrC is small because of thin ZrC layer

Separation of MWCNTs To Prevent Agglomeration

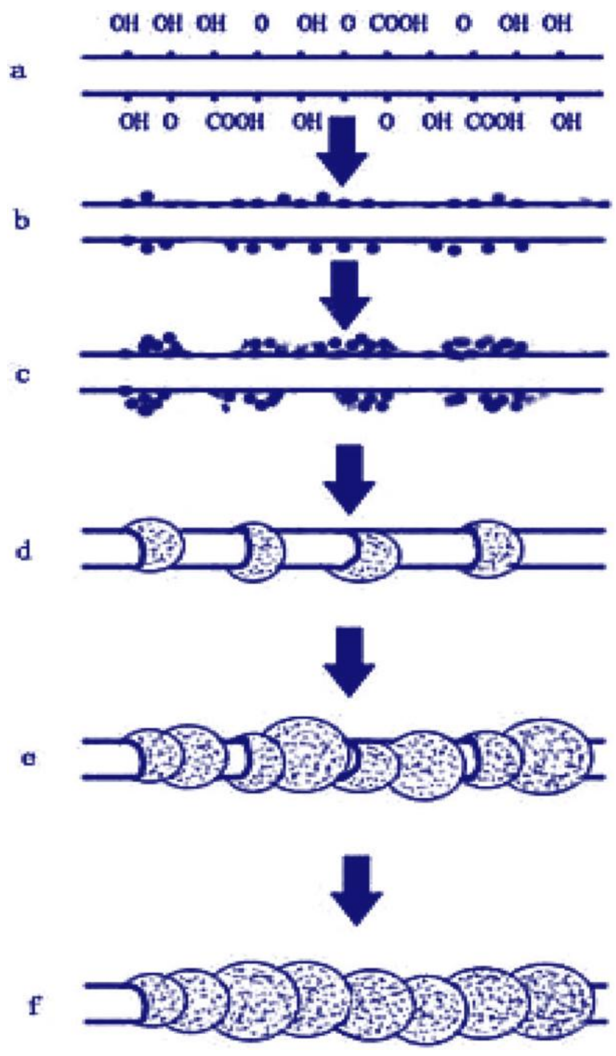
Carboxylated MWCNTs disperse well in acid media



- Surface-carboxylation of MWCNTs by acid treatment in 1:3 HNO_3 :H_2SO_4, sonication for 1 h and then kept at room temperature for 24h. This process provides MWCNTs with more –COOH chemical groups on the surface and reduce the agglomeration of MWCNTs.

- Acid treated CNT is used for chromium coating by electroless plating (wet chemical method)

Electroless Coating
(Schematic – UAB)



Acid treated or Carboxylated MWCNTs

Sensitization by (0.1 M $SnCl_2$ + 0.1 M HCl) sonication for 1h

Activation by (0.0014M $PdCl_2$- 0.25MHCl for 30 min)

Electroless deposition of Chromium from Chromium Acetate solution (2 days)

Reduction of the metal ions by Formaldehyde

By changing the metal salt solution concentration a uniform coating can be achieved

Coating of MWCNTs

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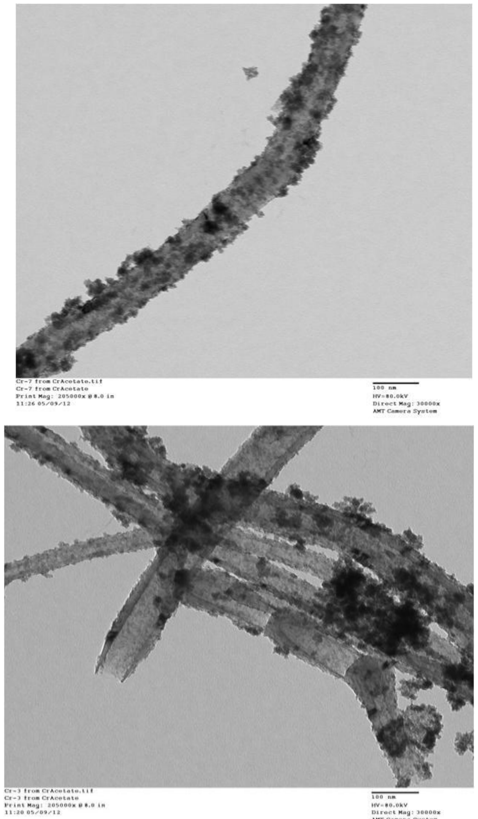
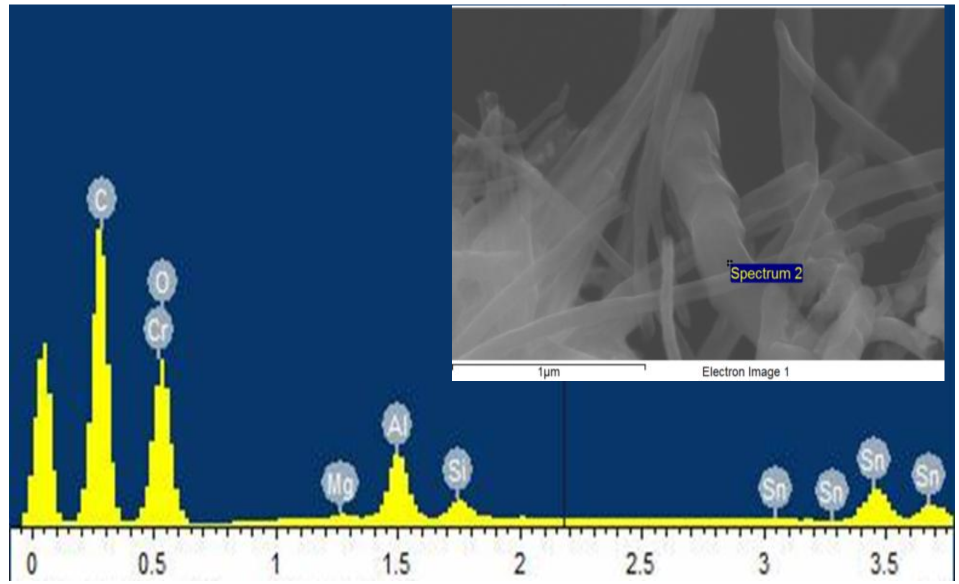


TEM images showing coating of metal from electroless coating method. ~20 nm thick layer of metallization can be observed in individual MWCNT surface



Representative EDS scan of chromium electroless plated MWCNTs. Inset shows the corresponding SEM image MWCNTs. Sn from sensitization step can also be seen. Other elements are from SEM sample holder.

Cr seems to oxidize during the coating process

MWCNT Thermal Conductivity

(Vanderbilt)

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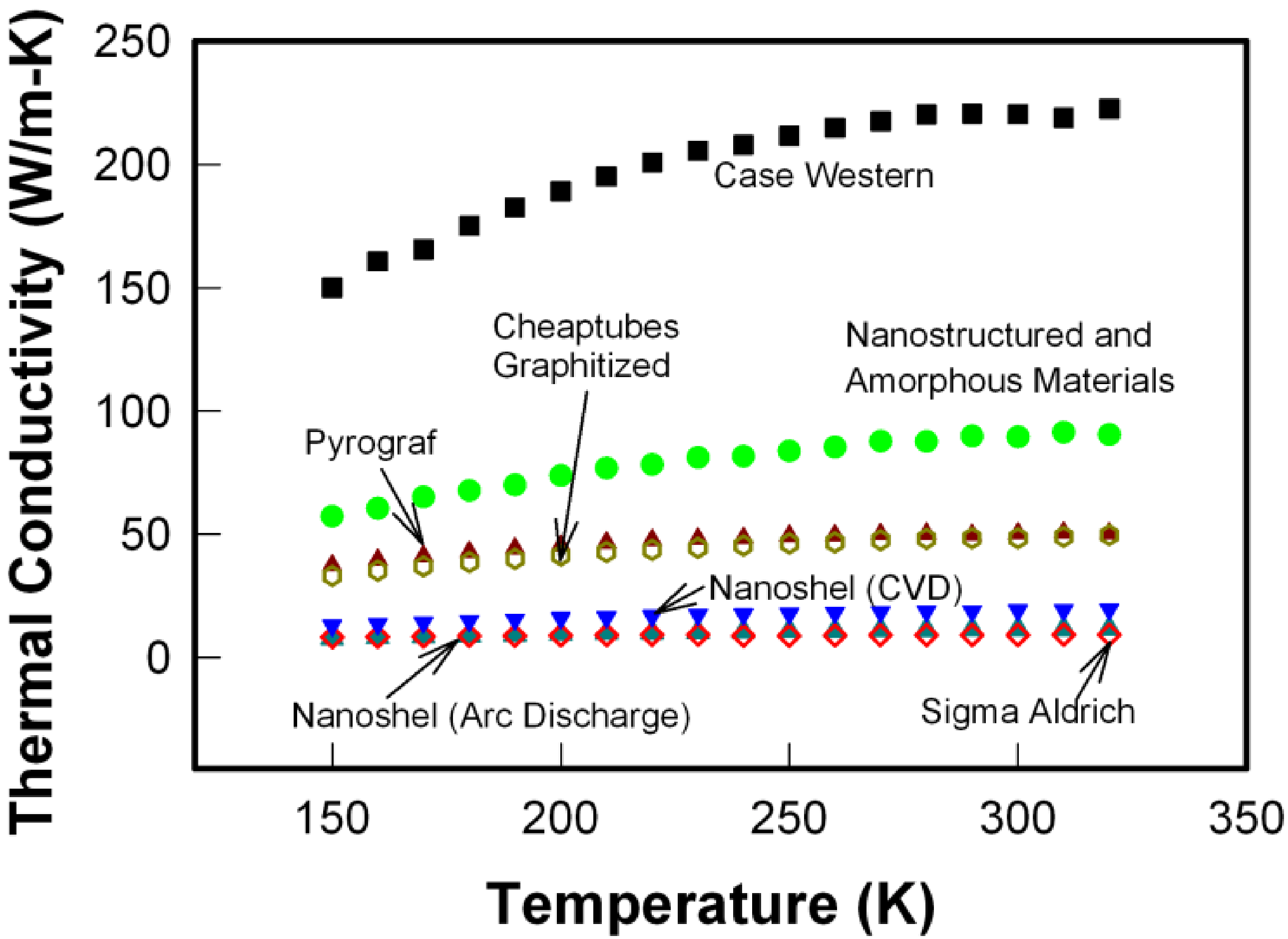
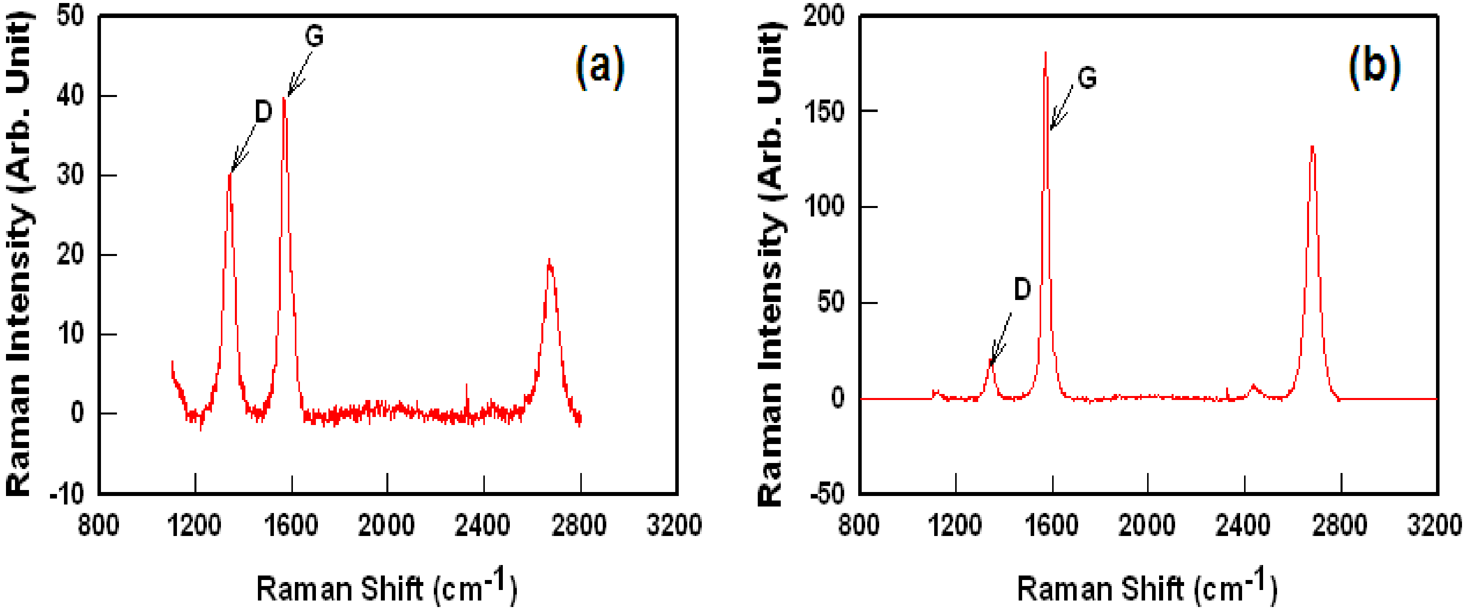


Note: Measured thermal conductivities were much lower than expected

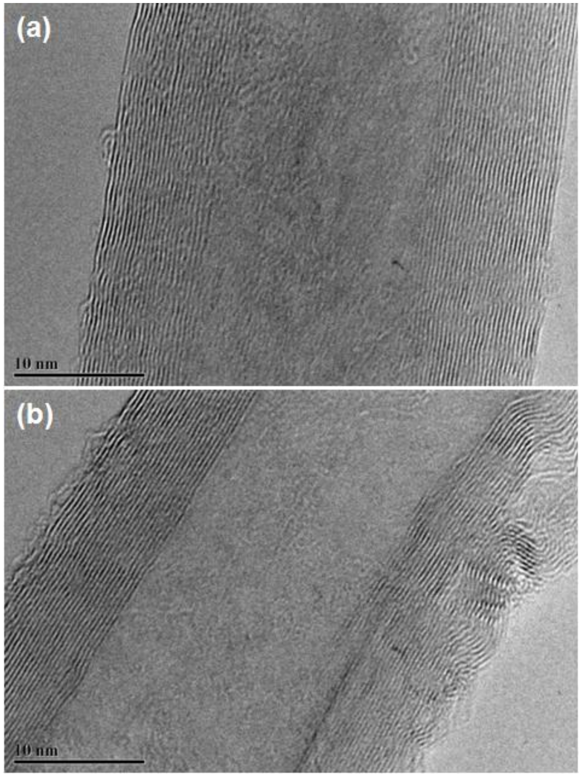
MWCNT Quality: Raman Spectroscopy



Raman spectroscopy results for (a) Nanoshel CVD MWCNTs with a large D/G ratio and (b) Cheap Tubes graphitized MWCNTs with a lower D/G ratio.

Note: D/G ratio should be near zero for high quality MWCNTs

MWCNT Quality: TEM Micrographs



TEM micrographs of a MWCNT at different positions. While the tube structure in (a) is good, there are significant structural defects in (b), which reduce the thermal conductivity.

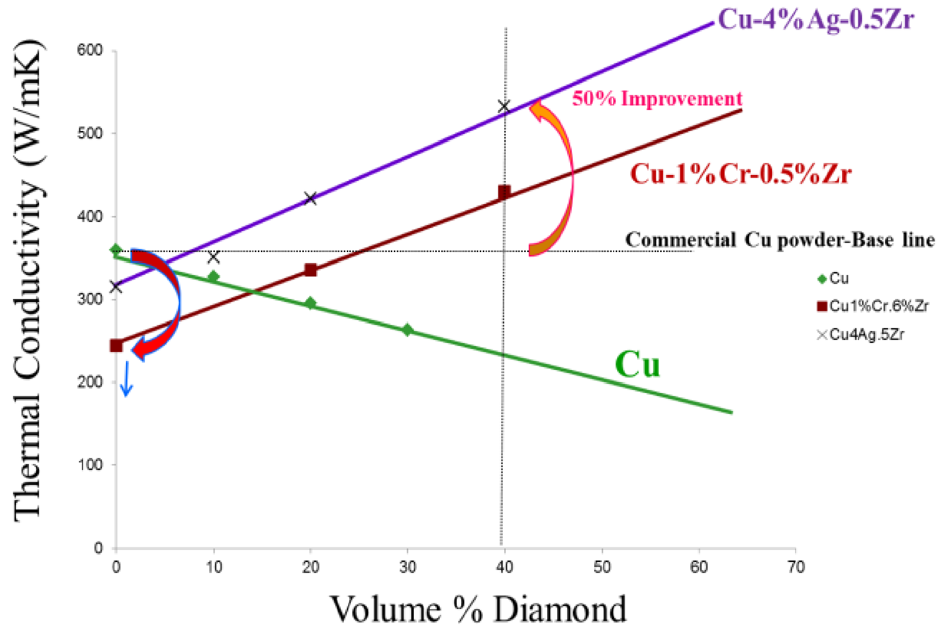
Discussion: NARloy-Z-MWCNT Composite

- Ball milling did not produce desired microstructure in NARloy-Z-MWCNT composite
  - MWCNT were not detangled -- they segregated in prior particle boundaries
- FAST process produced fully dense composites, but the tensile ductility was lower because of poor microstructure
- Thermal conductivities of NARloy-Z-MWCNT composites were lower than baseline

  -- Tangled MWCNT acted as insulators and lowered the thermal conductivity
- Thermal conductivities of commercially produced MWCNTs were much lower than expected
  - Attributed to poor quality of MWCNTs
  - Contributed to low thermal conductivity of NARloy-Z-MWCNT composites
- Separation of tangled MWCNTs by acid treatment was effective, but Cr electroless coating to keep them separated produced highly oxidized coatings, not suitable for bonding with MWCNT or copper
  - Should pursue alternate coating techniques such as pulsed laser deposition technique for coating Cr or Zr
  - Copper over coating will be necessary to prevent oxidation of coating and will also help to improve blending during ball milling

Discussion: NARloy-Z-D Composite

- Narloy-Z-D composites showed significant improvements in thermal conductivity (69% at 40vol%D)
  - Such improvements are not observed in Cu-D system
- ZrC at Cu-D interface is essential for good contact conductance
- The results support the quantum mechanics based model of contact conductance
- Further improvement in thermal conductivity is possible by coating diamond with Zr by pulsed laser deposition technique and then over coating with copper



Thermal conductivity of copper-based alloy-diamond composites

Recommendations

- Approach to improving the thermal conductivity of NARloy-Z-MWCNT composites should be changed for better results
  - Must use the highest thermal conductivity MWCNT (>2000 W/m-K)
  - Reliable source for high thermal conductivity MWCNT must be found
  - MWCNT clumps should be separated and coated with a carbide former such as Zr or Cr and then over coated with copper for best results
  - Dry techniques such as pulsed laser deposition should be used for coating the MWCNTs
- NARloy-Z-D system looks promising for further development for application in advanced rocket engines
  - Further optimization of diamond particle size and NARloy-Z-D interface is recommended
  - Development of mechanical property data is necessary for designing components
  - Demonstration at component level should be the next logical step