Plasma Processes, Inc.

Lightweight Beryllium Free Nanostructured Composites

SBIR Contract DASG60-02-P-41

Phase I Final Report

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Submitted by

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Introduction

- Beryllium (Be) has been used for aerospace and nuclear structures due to its lightweight, high stiffness, low CTE and high thermal conductivity.
- Despite its usefulness, beryllium is not an ideal material as it is expensive and inherently brittle. Moreover, Be poses a severe health hazard due to its toxic behavior resulting in chronic beryllium disease (CBD)- an irreversible and sometimes fatal scarring of the lungs
- There is a need to develop a non-toxic lightweight Be-free alloy, which has similar material properties as that of beryllium and can be fabricated easily.
- In the present study, novel lightweight and nanostructured Be-free composites have been developed and fabricated into near net shapes using plasma spray forming techniques.

Approach

- Hypereutectic Al-Si alloy was reinforced with nano size Al_2O_3 and carbon nanotubes to develop a composite having material properties similar to Be.
- The presence of nanograins and nano dispersoids would significantly improve the strength whereas Al_2O_3 will provide a high specific stiffness.
- Vacuum Plasma Spraying technique was adopted to fabricate near net shapes of Be-free alloy.
- Plasma Processes Inc. and Center for Nanoinitative, University of Central Florida formed a team to develop Be-free Nanostructured Composites.

Properties for Lightweight Materials

Material	Density lb/in^3	Micro-Yield KSI	Specific MicroYield KSI/lb/in^3	Elastic Modulus MSI	CTE 10-6/°F
Hypereutectic Al-Si	***0.098***	***>18***	***184***	***15***	***8.6***
Alumina	***0.133***	***30***	***208***	***53***	***4.2***
Al/SiC MMC	0.106	17	160	15	7.4
Beryllium (I-70)	0.067	2.5	37	42	6.3
Al 6061-T6	0.097	9.4	97	9.9	13.1
Mullite Ceramic	0.101	16	158	10	3.3

Selection of Materials

- Hypereutectic Al-Si (Vanasil) was chosen as *matrix* material due to its lightweight, high stiffness, high thermal conductivity and non toxic nature.

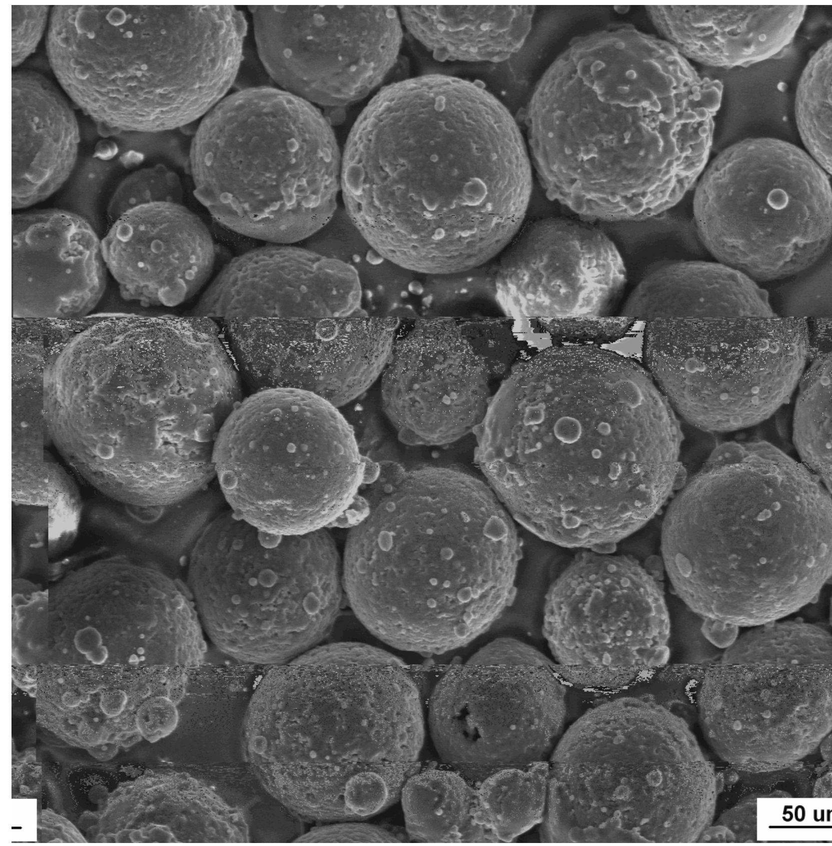
- Nanostructured Aluminum Oxide was chosen as the *reinforcement* as its nanosize will increase the strength where as Aluminum oxide ceramic will increase the stiffness

Carbon Nanotube Reinforcement

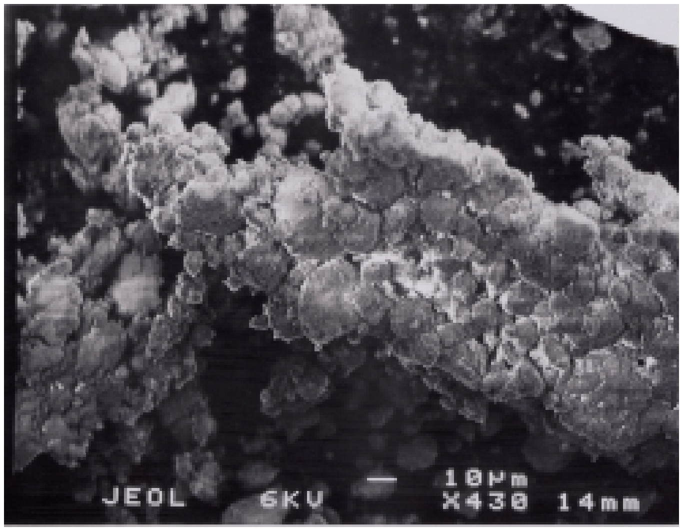
- Carbon Nanotube (CNT) is the ideal reinforcement for nanocomposites as they possess extraordinary mechanical properties with a strength of 11-200 GPa and elastic modulus of 270GPa-1 TPa (strength 1000 times more than Be and specific stiffness twice that of Be).
- Plasma spraying of carbon nanotube composites is a unique and unexplored area of research which has never been reported in literature.
- Multiwalled Carbon Nanotubes were also added as the *reinforcement* to Vanasil matrix to synthesize a novel nanocomposite.

Vanasil Powder: Matrix Material

- Gas atomized hypereutectic Al-Si (vanasil) powder (-45 micron) with the purity greater than 99% was the matrix material.
- Spherical powder has good flowability which is essential for consistent feeding during material deposition using spray forming technique.

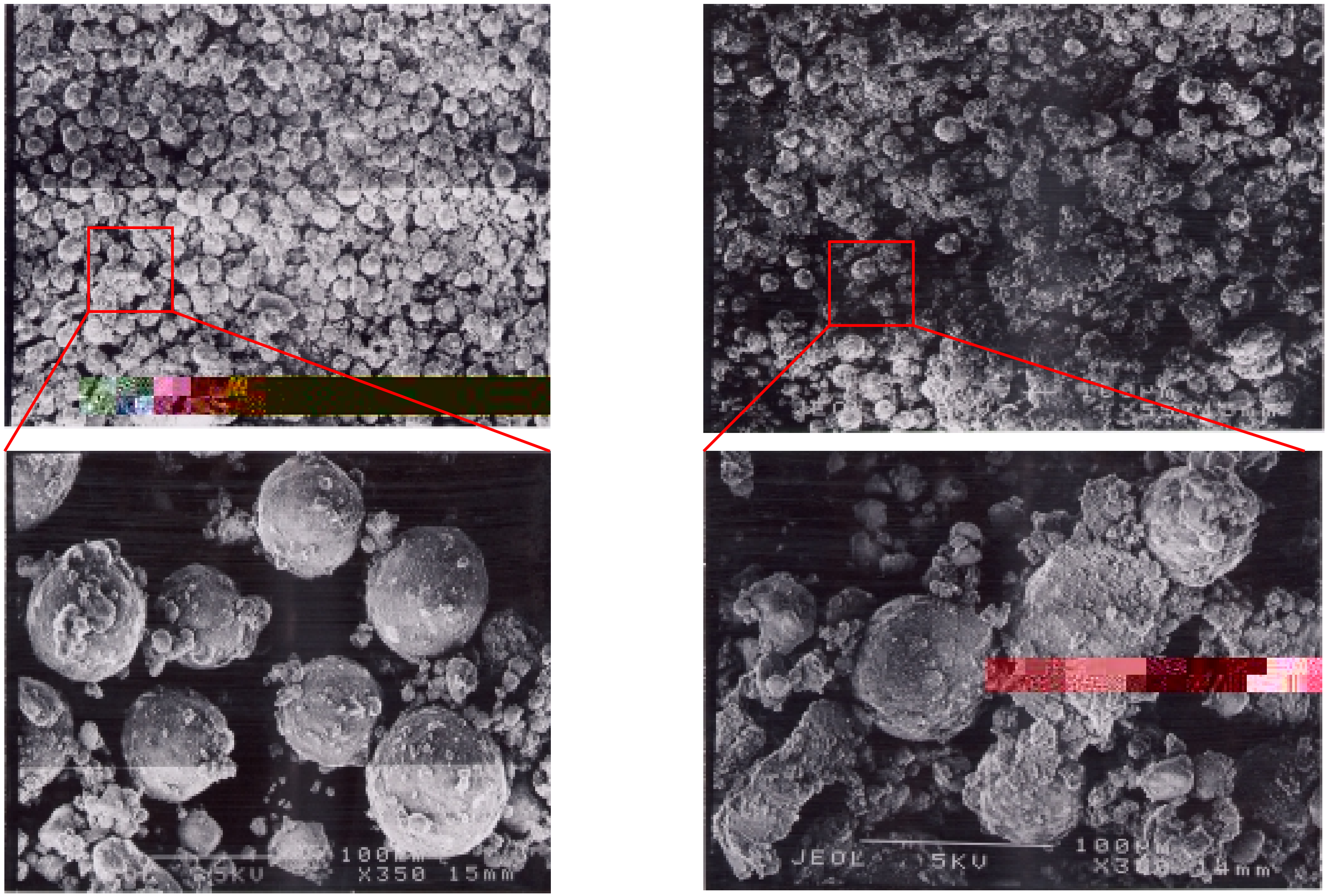


Nanostructured Al_2O_3 Used as Reinforcement



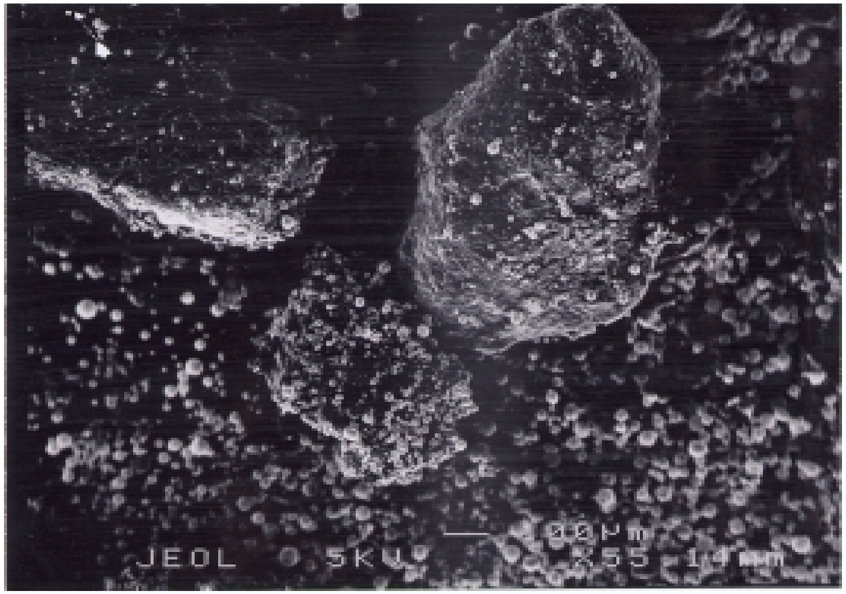
- Nanostructured Al_2O_3 (to be referred as NTA hereafter) with average grain size 30-70 nm was procured as loosely bound agglomerates.
- NTA was blended with Vanasil powder in two different compositions viz. 20 and 30 wt.% respectively.
- The blended powders were mixed in a ball mill for 48 hours to promote homogeneous mixing.
- The blended powders were identified as V+20NTA and V+30NTA

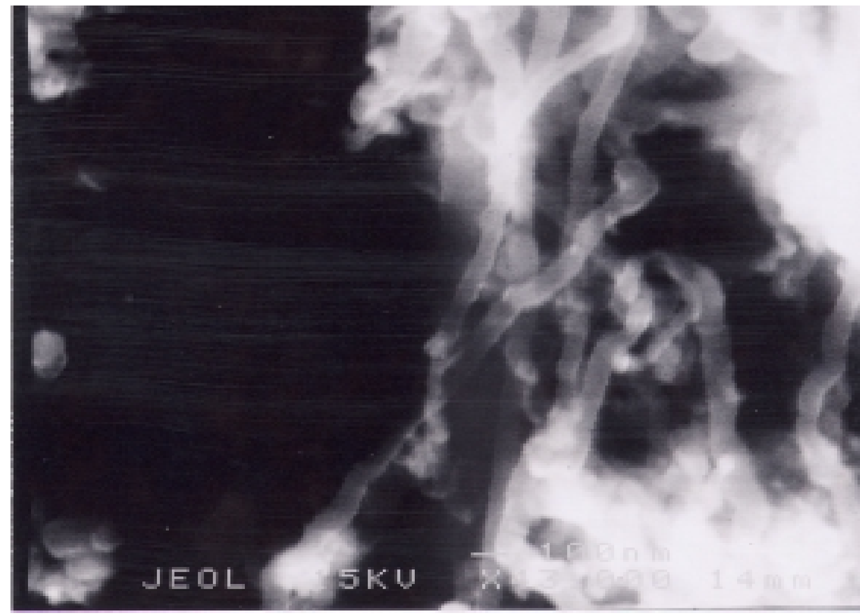
Blended Vanasil +20 NTA Powder (left) & +30 NTA (right)



- NTA powder is homogenously blended with Vanasil powder

Blended Vanasil +10 CNT Powder





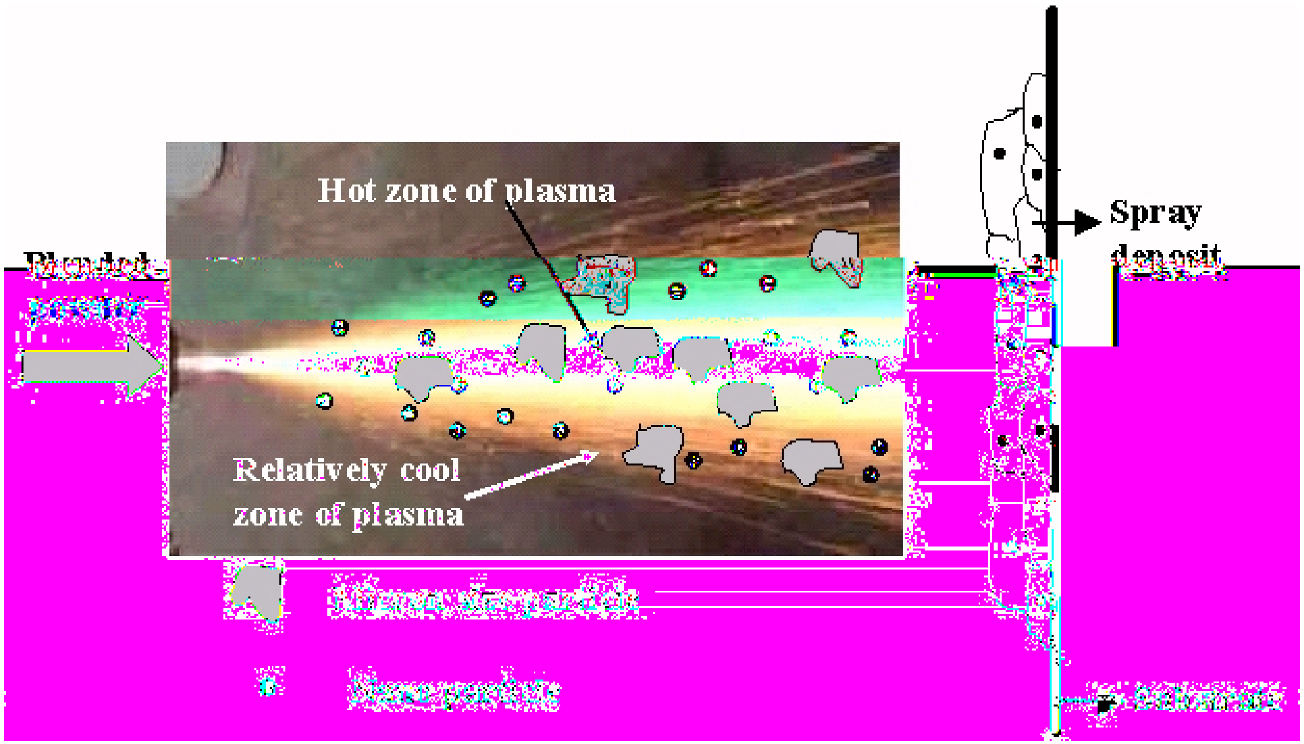
- The agglomerate blended powder formation (top and left) and the nanotube structure (right)

Blended Powders: WHY?

- A mixture of nanosize and micron size powder will enable easier flow of feedstock powder in the plasma flame. It is extremely difficult to flow nanosize powder only due to its low mass and the resultant inability to be carried in a moving gas stream and deposited on a substrate.

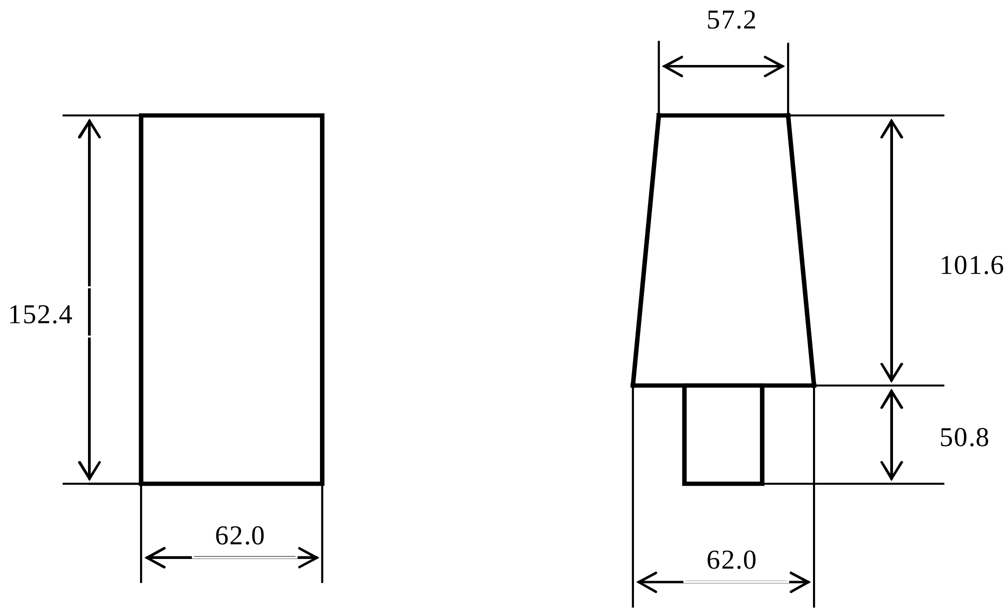
- In addition, with controlled plasma parameters, partially melted/unmelted nanosize agglomerates can be trapped between fully melted micron size powder particles to retain a higher degree of nanostructured particles in the spray deposit.

Trajectory of Micro + Nano Blended Powders Through Plasma



- A larger degree of melting occurs in micron size particles because they flow coherently through the hot zone of the plasma. On the contrary, a larger fraction of nanosize powder agglomerates do not flow through the hot core of the plasma due to their smaller size. Hence, they are partially melted and trapped between the coarser particles.

Mandrel Material and Design



(a) Cylindrical mandrel

(b) Tapered mandrel

All dimensions are in mm

Schematic illustration of the mandrel designs: (a) Mandrel on left was used for fabricating tensile samples and metallurgical analysis samples and (b) tapered mandrel was used to spray form thin walled structures

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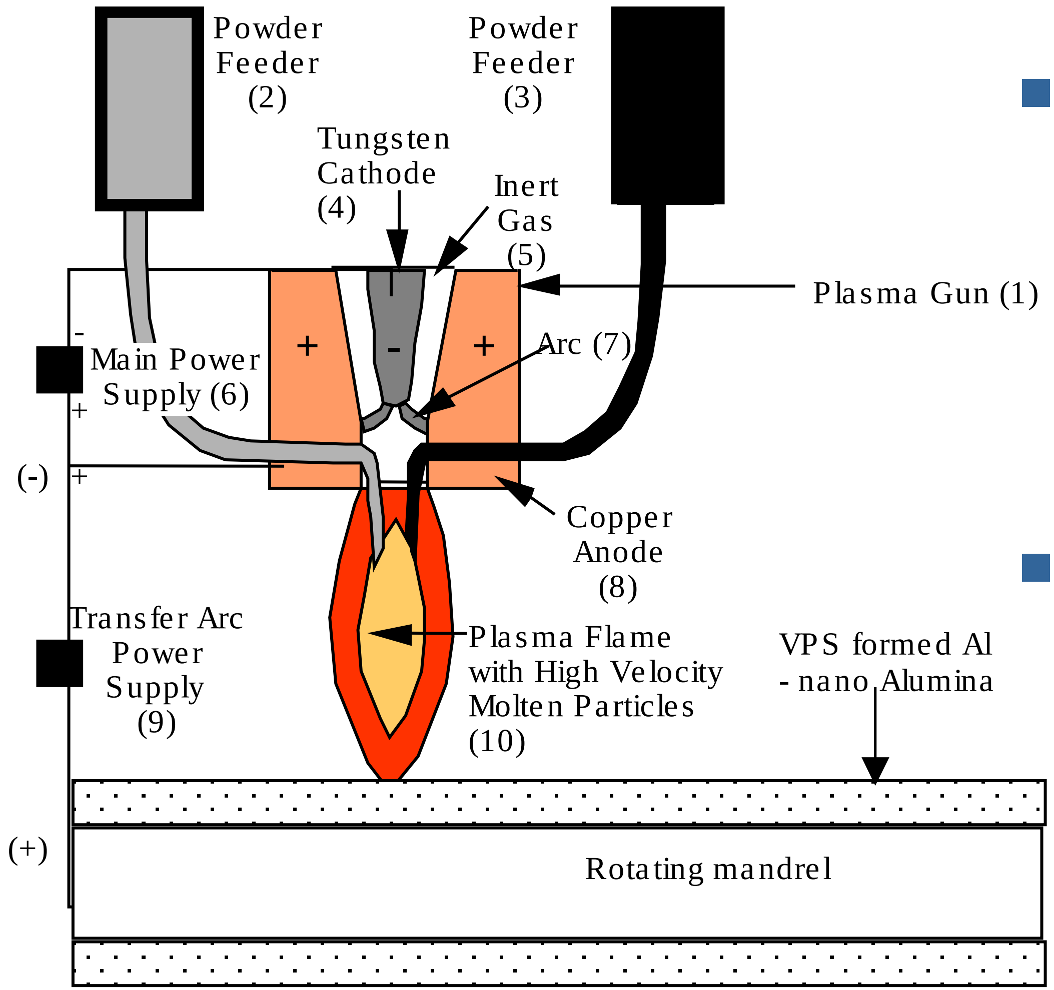
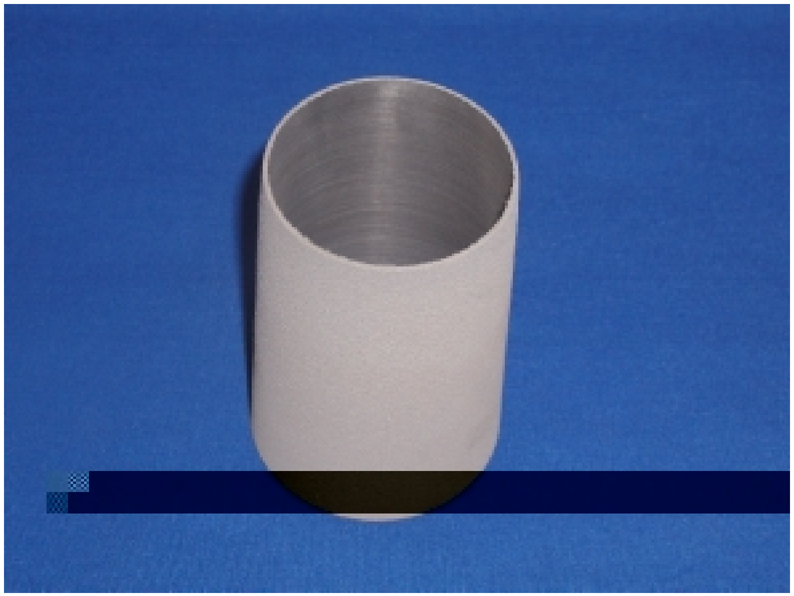
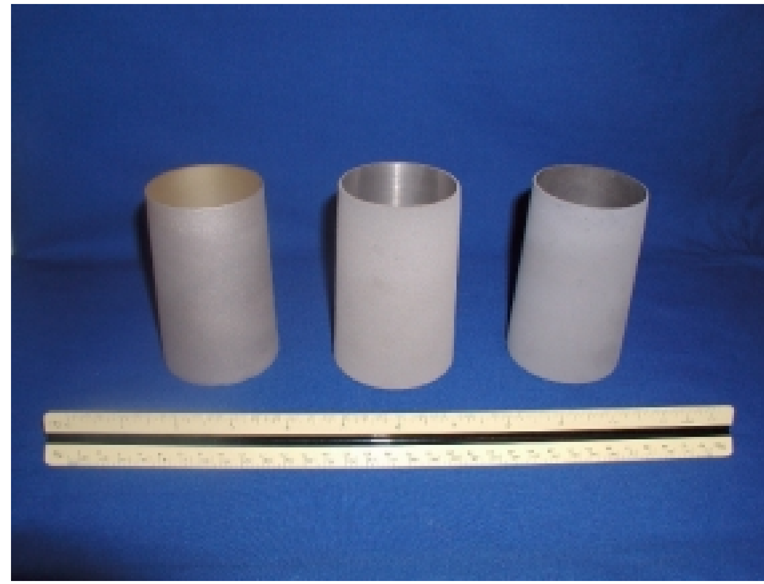
Vacuum Plasma Spraying



- Vacuum Plasma Spraying was adopted to spray Vanasil, Vanasil+20NTA and Vanasil + 30NTA powders on 6061 Al mandrels.
- Vanasil +30NTA powder displayed flow problems due to higher volume fraction of nanosize powder.

Vacuum Plasma Sprayed Vanasil





- 62 mm diameter and 100 mm tall tapered Vanasil shells (1-2 mm thick) were spray formed using VPS technique.
- Multilayered shells can also be fabricated. Picture on right shows first cone with an internal Al-Bronze layer.
- Vanasil was also sprayed on 62 mm diameter straight mandrels to fabricate tensile samples.

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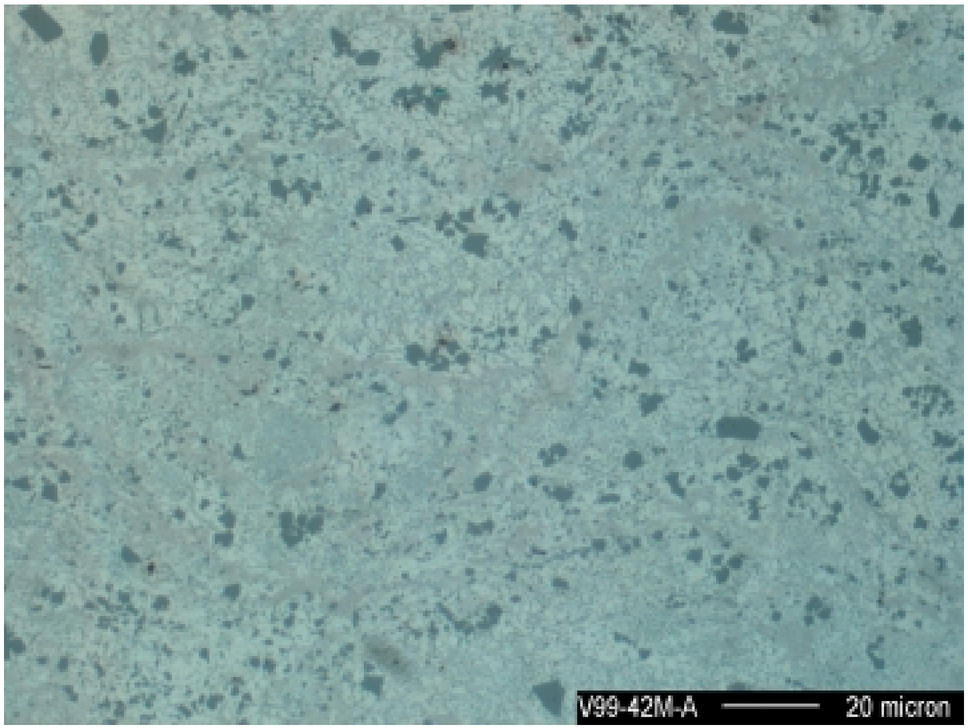
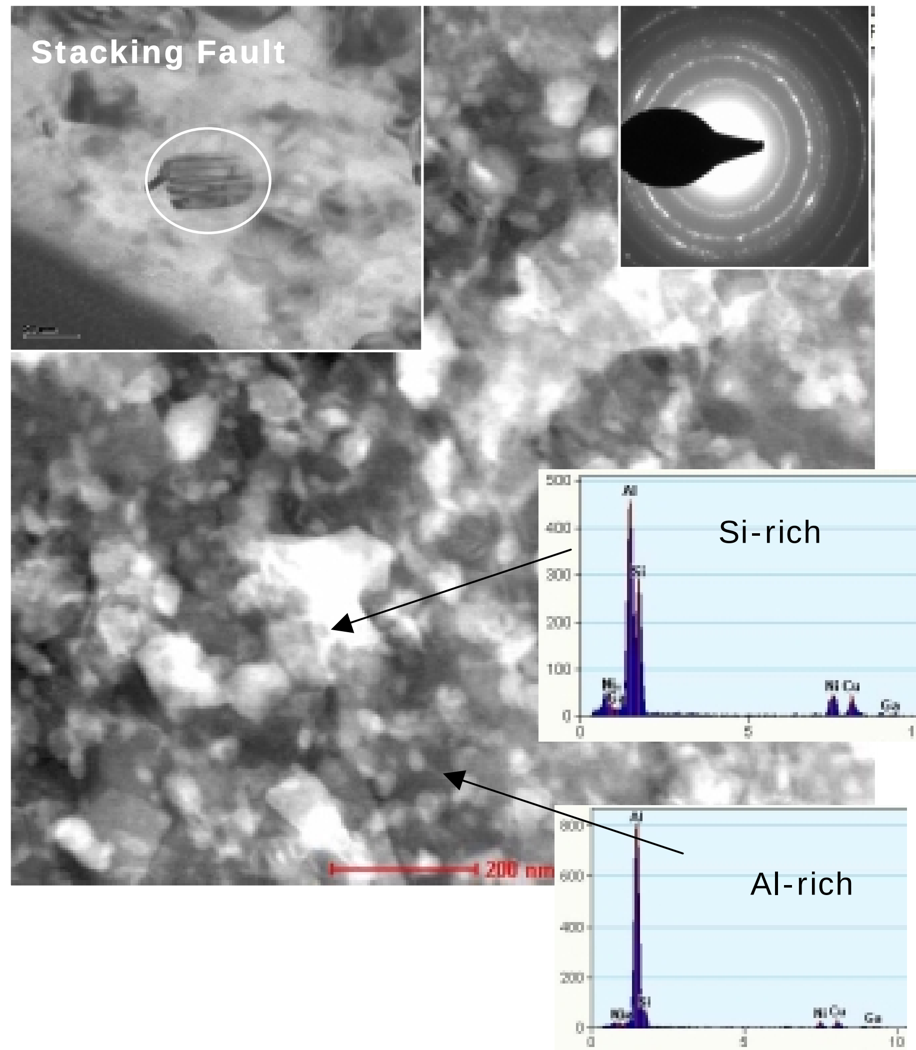
Vacuum Plasma Sprayed Vanasil



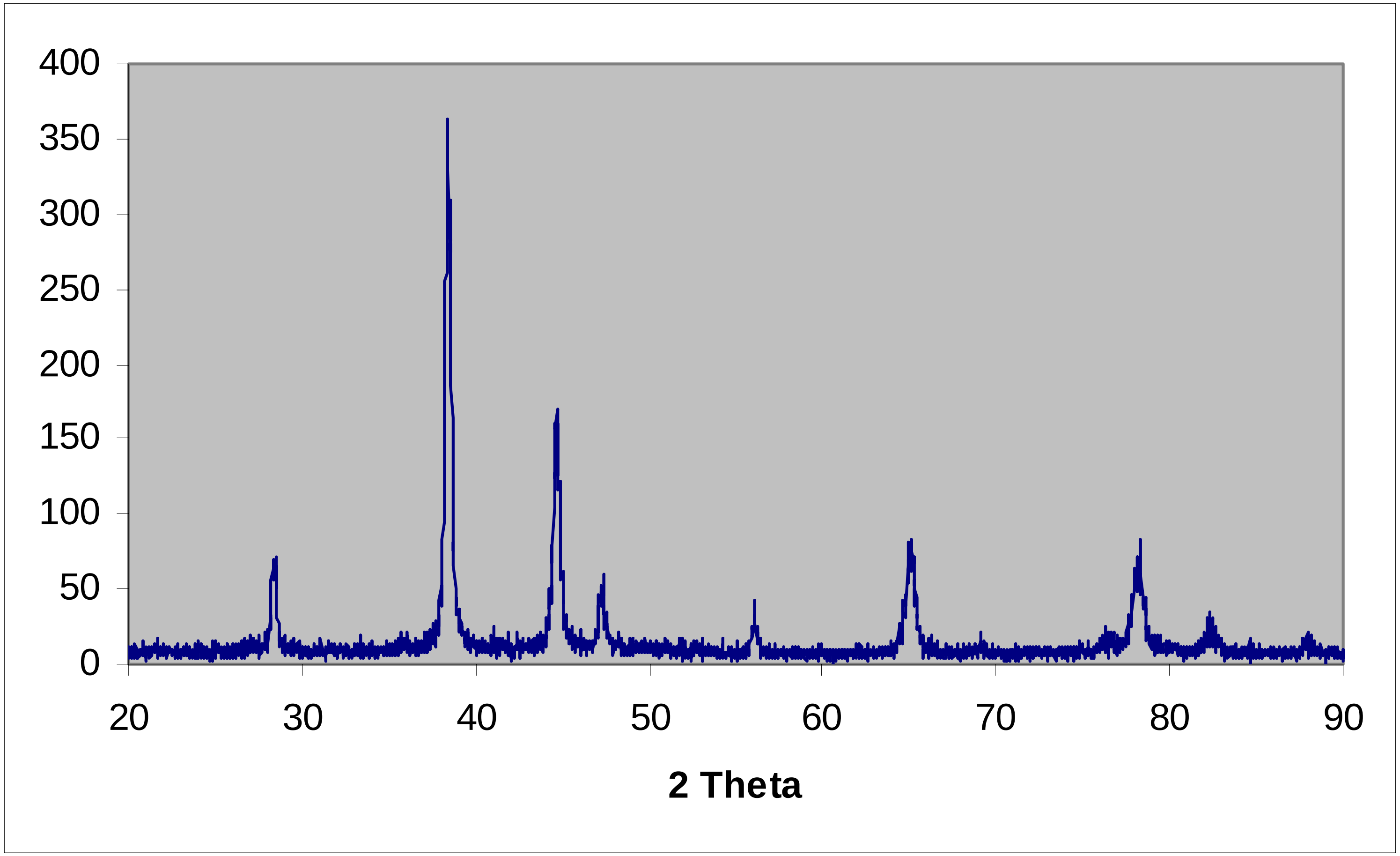
- Highly dense microstructure in as-sprayed condition
- Homogenous distribution of fine Si particles ($\leq 5\mu m$)
- Innovative mandrel cooling resulted in formation of nanostructure as revealed by TEM analysis.

TEM Analysis of VPS Vanasil

- Average grain size of VPS Vanasil < 50 nm. Innovative substrate cooling results in rapid solidification where grain nucleates rapidly but do not have sufficient energy for growth.
- EDS Analysis shows homogenous distribution of Al and Si in the spray deposit.
- Tensile strength of Vanasil: 345 MPa (50 ksi) in as-sprayed condition. Elastic Modulus ~ 80 GPa sent.
- High tensile strength of as-sprayed Vanasil is due to (a) high degree of nanostructure in the deposit (b) homogeneous distribution of ultrafine Si particle and (c) formation of stacking faults which impede the dislocation movement.



X-Ray Diffraction of VPS Vanasil



- VPS Vanasil X-Ray diffraction plot peaks align quite snuggly with that of synthesized Aluminum PDF #04-0787

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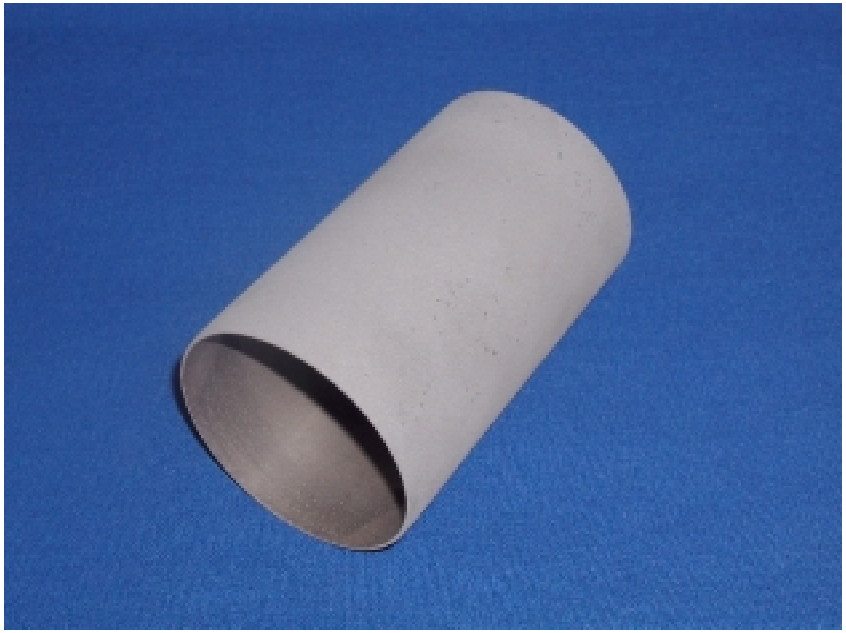
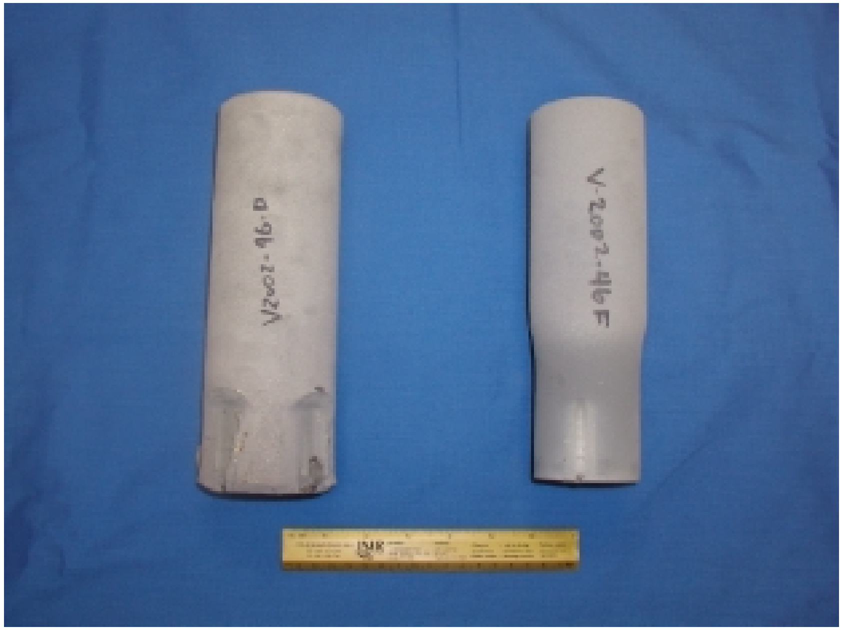
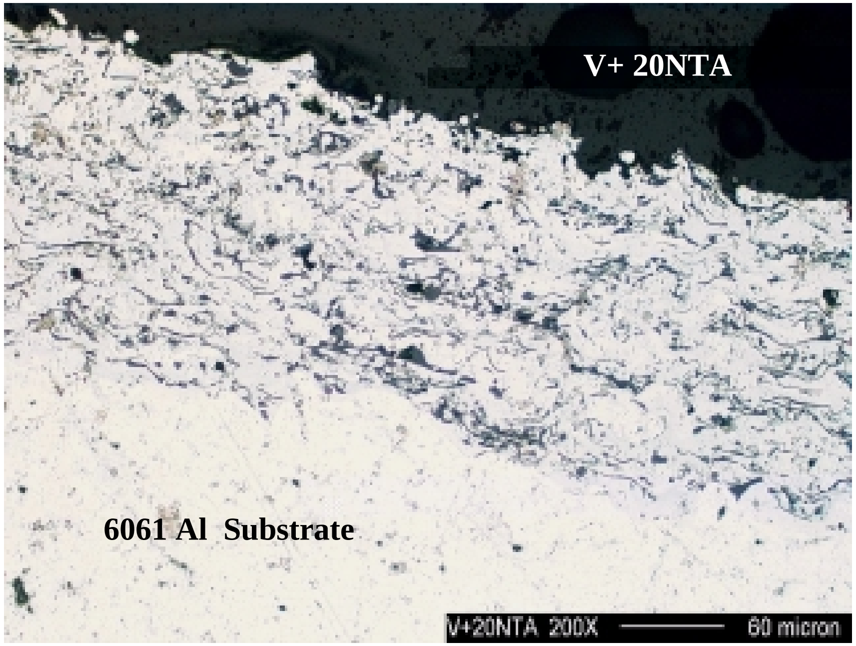
Vacuum Plasma Sprayed Vanasil+20NTA





- 62 mm diameter and 100 mm tall tapered (~1-2 mm thick) Vanasil+ 20NTA shells were spray formed using VPS technique.
- Vanasil +20NTA was also sprayed (~ 3.5mm thick) on 62 mm diameter straight mandrels to fabricate tensile samples.

Vacuum Plasma Sprayed Vanasil+20NTA



- The black splats are aluminum oxide reinforcements in the spray deposit.
- It was extremely difficult to distinguish between the black colored reinforcement and the porosity by quantitative image analysis.
- Hence, water immersion technique was employed to determine the density (96% of theoretical density) of the VPS Vanasil+20NTA.

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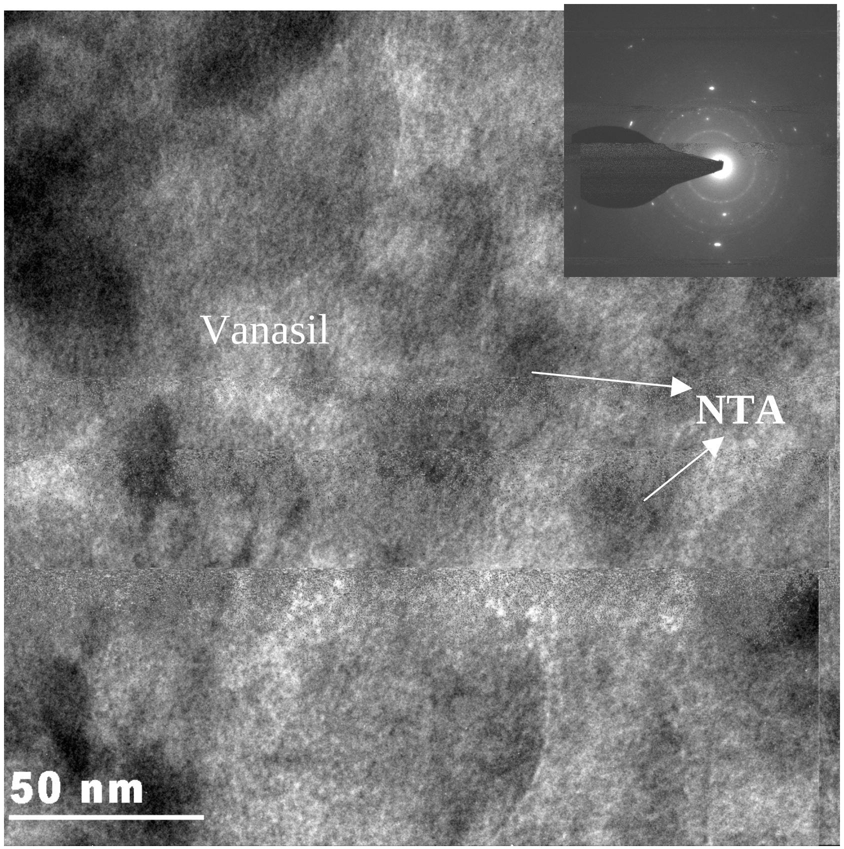
TEM Analysis of VPS Vanasil + 20NTA



- Vanasil+20NTA possess and retain nanostructure after plasma spraying.
- Black colored reinforcements are NTA (20-50 nm in size) whereas light gray color is Vanasil matrix.
- SAD pattern shows both ring and spot patterns.
- EDS spot analysis confirms presence of NTA and Vanasil (next slide).
- Tensile strength tests and elastic modulus measurements are being done at present.

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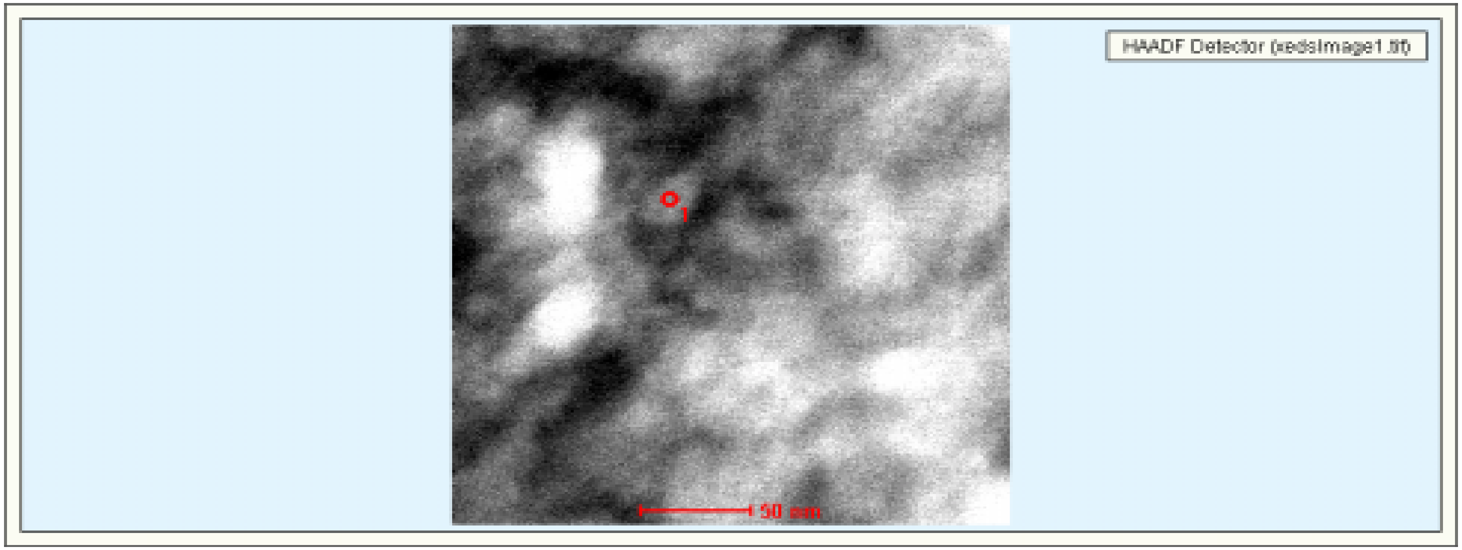
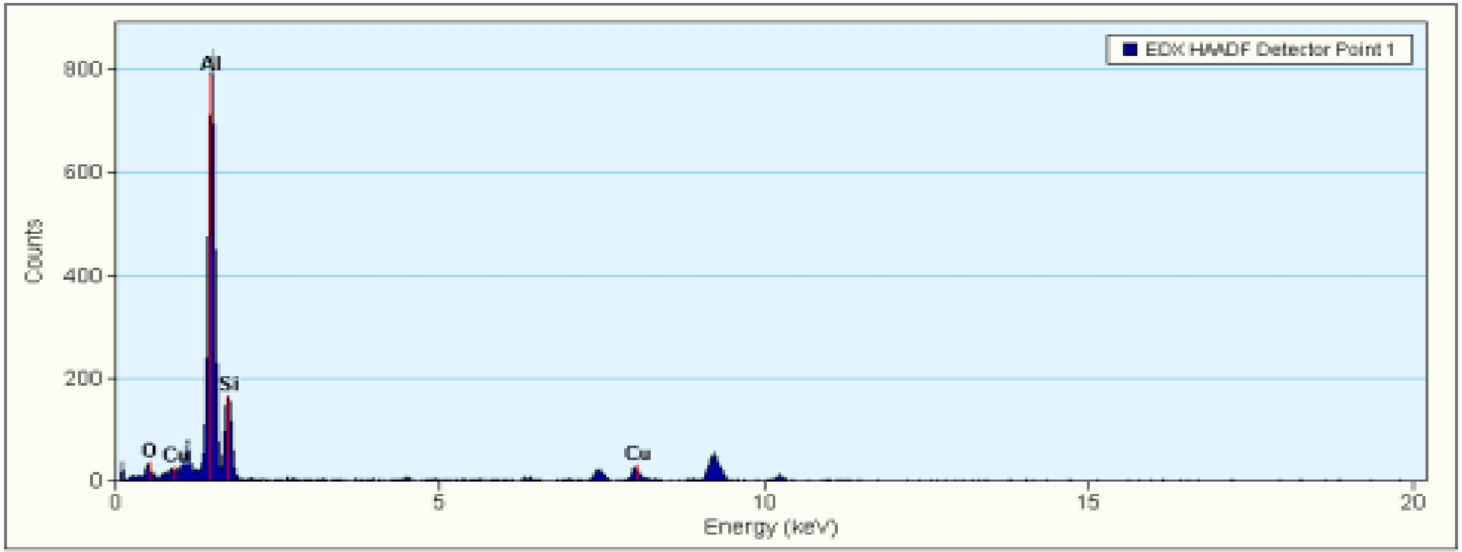
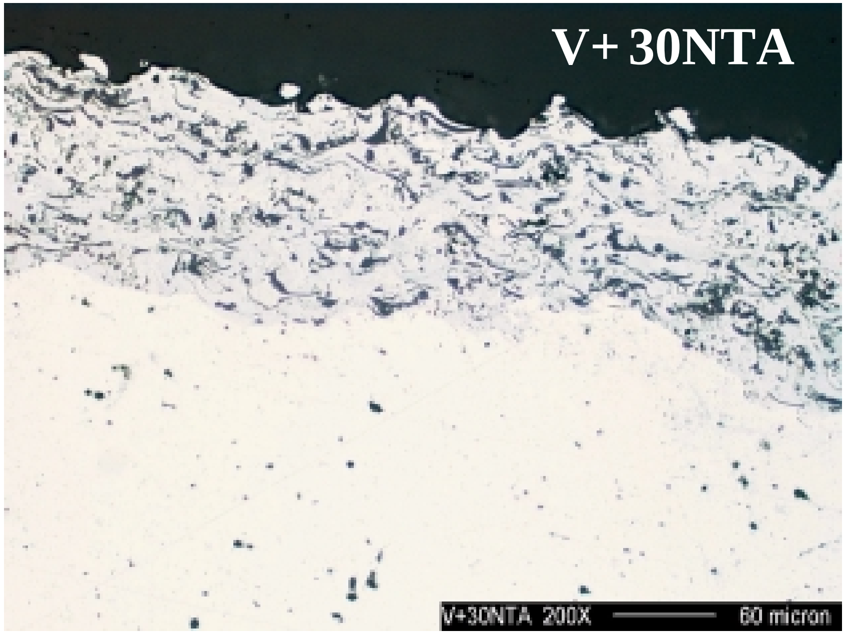
TEM-EDS Analysis of VPS Vanasil + 20NTA





Vacuum Plasma Sprayed Vanasil+30NTA



- The black splats are aluminum oxide reinforcements in the spray deposit.
- Powder feedstock for V+30NTA consists a higher fraction of nanosize particle reinforcements which resulted in the poor powder flow behavior and subsequent clogging of the gun.
- A higher fraction of nanoparticles were lost as overspray during the trajectory from gun to the substrate due to relatively low mass and subsequent inability to flow.
- V+30NTA Density (93.8% of theoretical density).
- Tensile samples could not be fabricated due to powder flow problems and inability to spray thick deposits.

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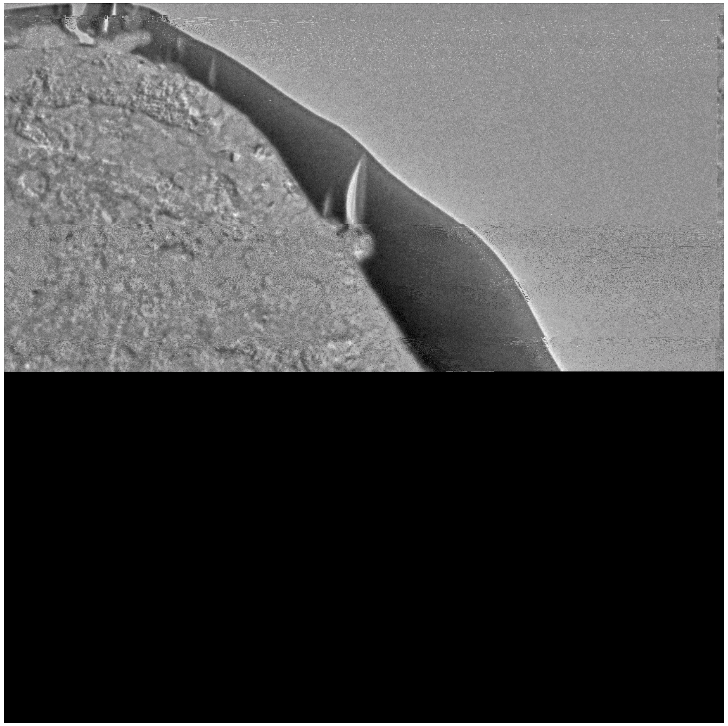
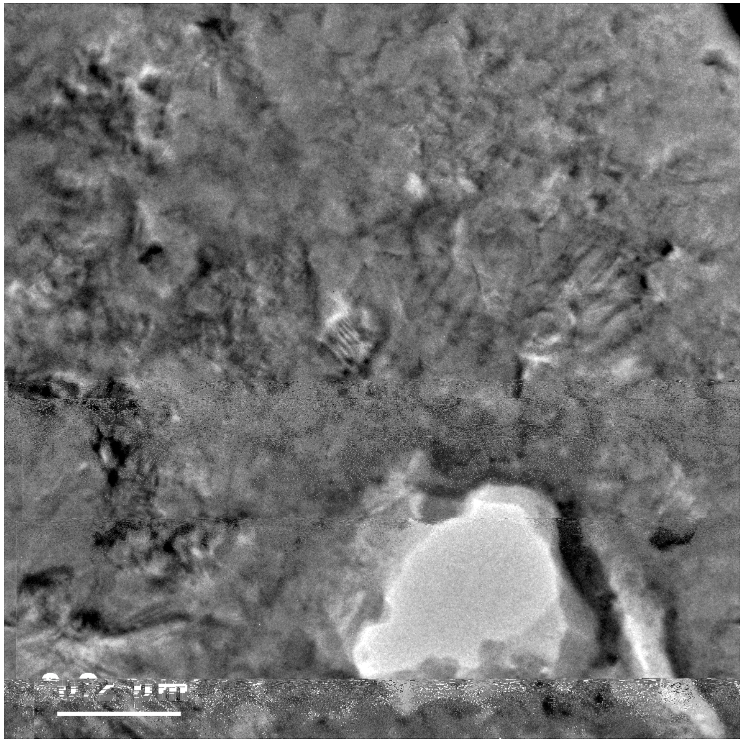
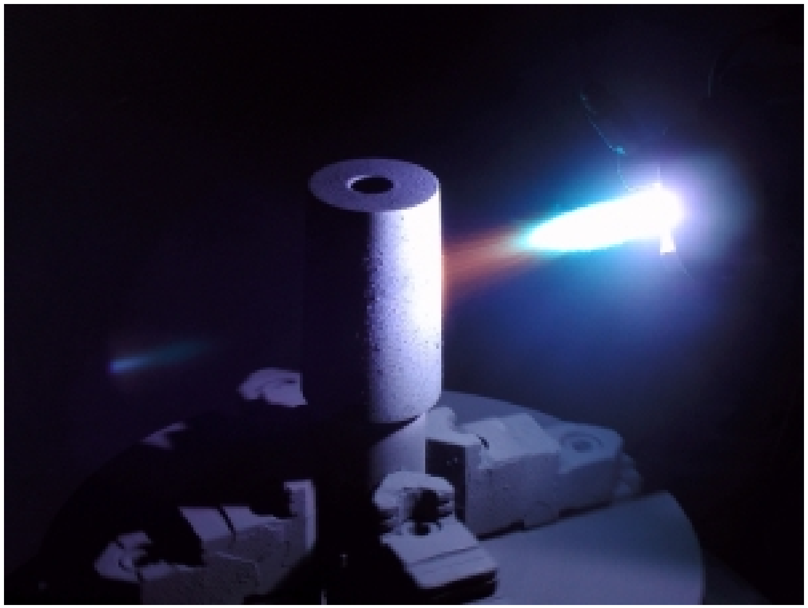
TEM Analysis of VPS Vanasil + 30NTA

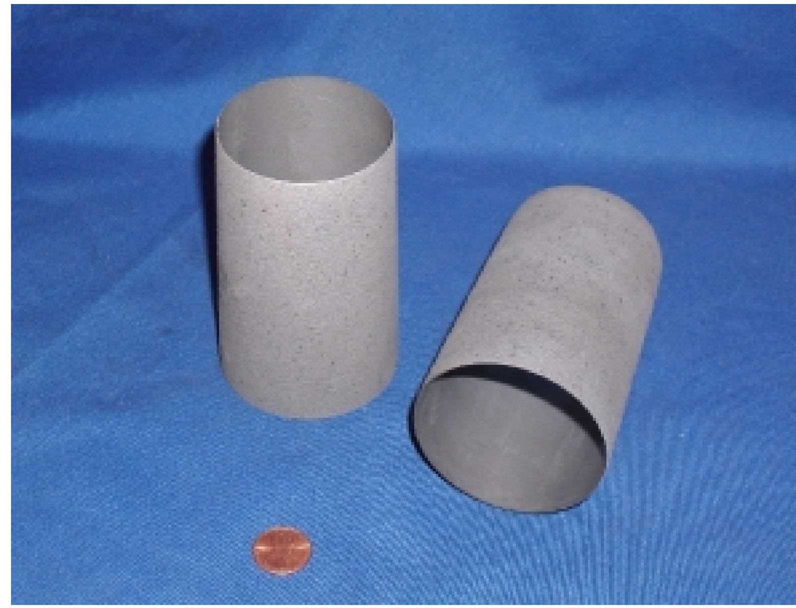




• Highly porous structure due to poor flow behavior of feedstock powder and overspray of nanostructured powder.

Air Plasma Sprayed (APS) Vanasil +10 CNT Structures





- 62 mm diameter and 1 mm thick tapered cylindrical nanocomposite shells (right) have been successfully spray formed using APS technique (left).
- Blended powder displayed inconsistent flow behavior due to the entangled clusters of carbon nanotubes.

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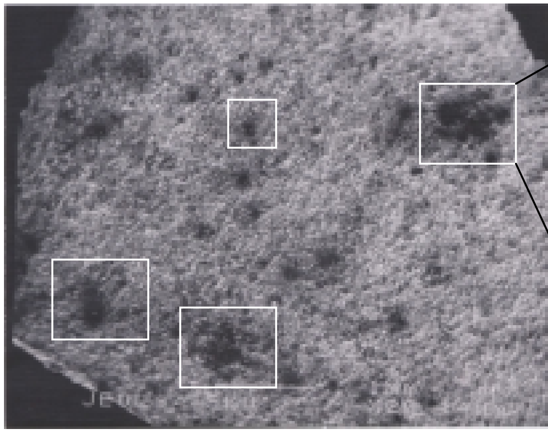
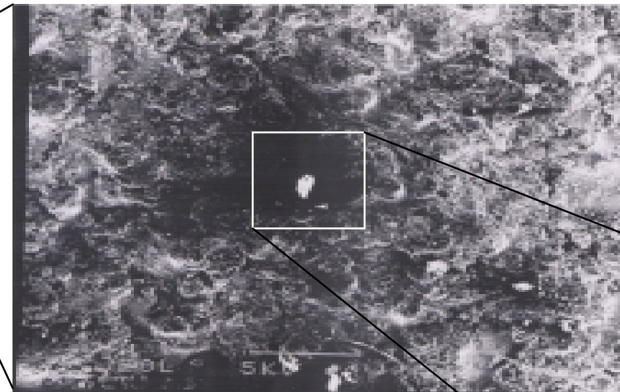
SEM Analysis of As-Sprayed Vanasil +10CNT





- Diffusion of CNT on surface, seen as black regions with white dots in the center (above). CNT were not observed in the spray deposit.
- Possible formation of an allotrope of Carbon on surface of Vanasil by high temperature and pressure that was present during plasma spray (right).
- The study of mechanical and thermal properties of these nanocomposites will be done in Phase II efforts.

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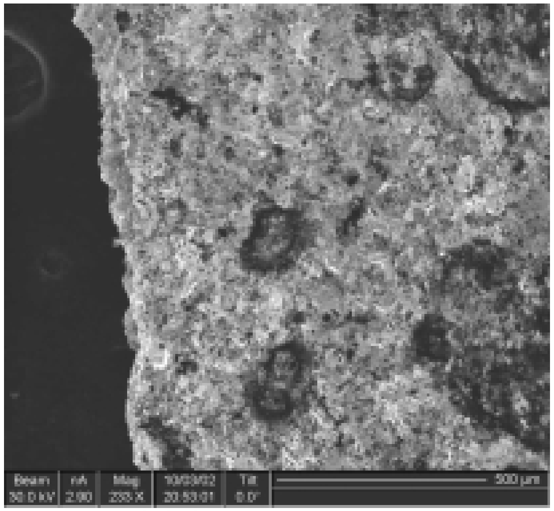
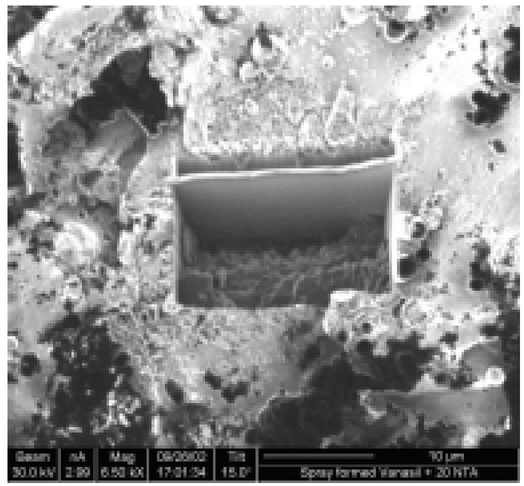
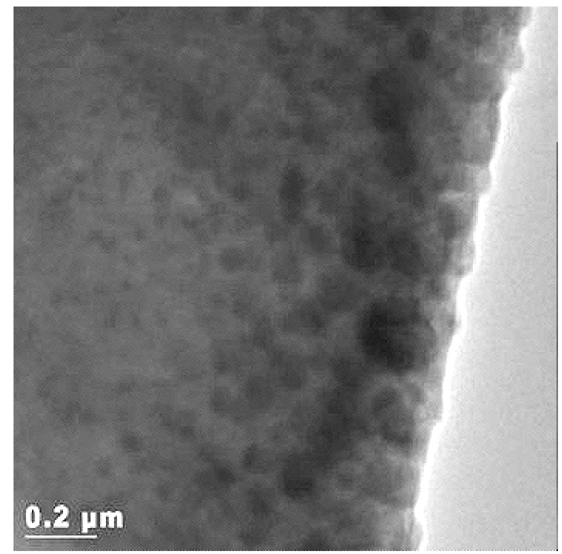
TEM Analysis of As-Sprayed Vanasil +10CNT



Black regions are clusters of CNT



FIB lift out from as-sprayed Vanasil + 10CNT



Ultrafine grain size (100nm) in as-sprayed Vanasil +10CNT

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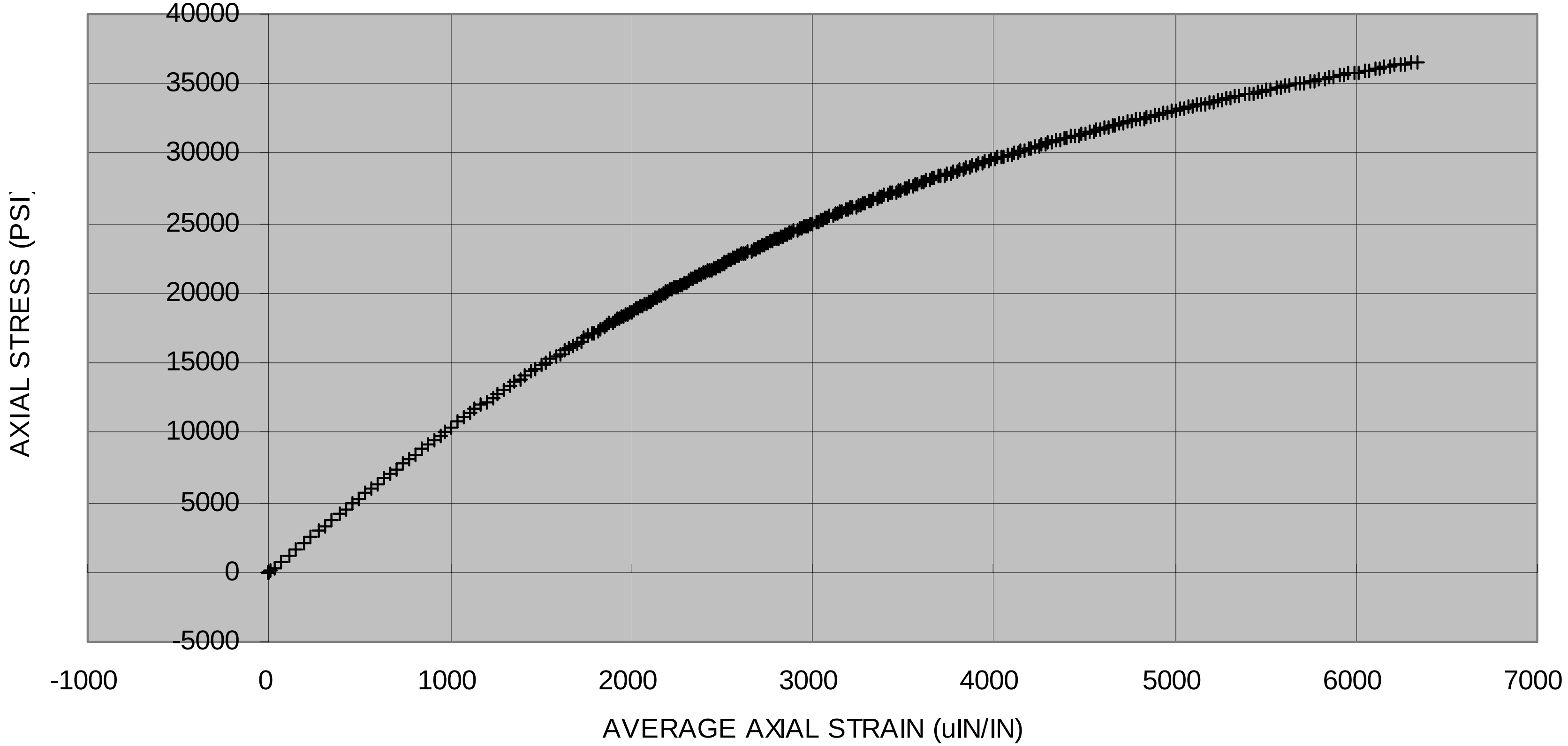
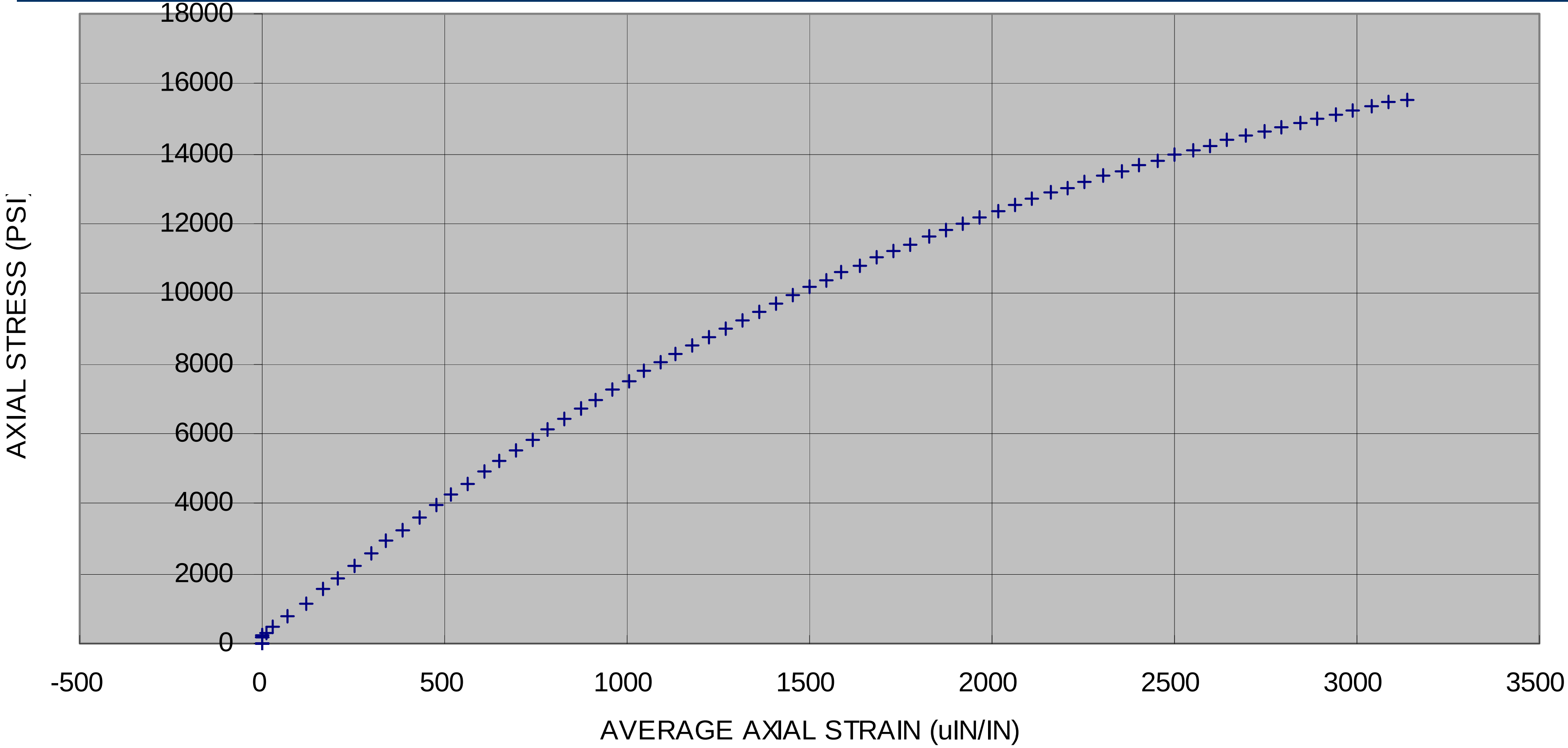
Vanasil (Axial Stress vs. Axial Strain)



- Fracture Strength ~ 37 ksi (255 MPa)
- Elastic Modulus~ 10.8 Msi (74 GPa)

Vanasil+20NTA (Axial Stress vs. Axial Strain)



- Fracture Strength: 16 ksi (110 MPa)
- Elastic Modulus: 9 Msi (62 GPa)

Low Strength with Nanostructured Alumina (NTA) Reinforcements? Why and What Next?

- A higher degree of porosity was observed in the initial spray deposited Vanasil +20 NTA samples at the matrix/reinforcement interface. Even though nanostructure was retained in the plasma sprayed deposit, porosity lowered the strength.
- There is a need to do further treatment to the blended Vanasil +20 NTA powder prior to plasma spray. These treatments would enhance the matrix/reinforcement bonding and reduce the degree of overspray which causes porosity.
- Such treatment could be i) spray drying of the blended Vanasil + NTA powder ii) spray drying of the nanostructured alumina powder and then blending with Vanasil and iii) spray drying of the nanostructured alumina powder, followed by thin metallic coating on spray dried powder particles and then blending with Vanasil.

Comparison with Beryllium

Material	Density (g/cc)	Strength	Specific Stiffness (GPa.cc/g)	Therm. Cond. (W/mK)	Material Cost	Processing Cost	Health Hazard
Vanasil	2.75	255-340 MPa (expt.)	27-36 (expt.)	238 (expt.)	$	$	None
Vanasil +20 NTA	2.90	340-400 MPa (theoretical)	40-60 (theoretical)	To be done in Phase 2	$	$	None
Vanasil +10 CNT	2.60	1-2 GPa (theoretical)	60-120 (theoretical)	To be done in Phase 2	$$	$	None
Beryllium	1.80	434 MPa	150	200	$$$	$$$	Severe

Summary

- Vacuum Plasma Spraying technique has been successfully used to fabricate highly dense, near net shape structures of hypereutectic Al-Si composite reinforced with nano alumina.
- Powder pretreatment, feeding method and plasma parameters have been developed to spray nanosize powder.
- Microstructural analysis (grain structure, composition, phase distribution) of spray formed composite structure clearly indicates a high degree of retention of nanostructure in hypereutectic Al-Si composite reinforced with and without nano alumina.

Summary (contd.)

- Spray formed hypereutectic Al-Si shows a high fracture strength of 255-345MPa and elastic modulus of 74-80GPa without any plastic deformation. Such high strength is attributed to the presence of nanostructure and stacking faults.
- Phase I spray formed hypereutectic Al-Si composite reinforced with nano alumina had lower strength and stiffness due to porosity from non optimum deposits
- Preliminary investigations indicates that carbon nano tubes can also be used as reinforcement and spray formed into near net shape components.

Phase II Plans and Applications

- Fabrication of large size components- e.g. solar shade, flat and curved optics
- Investigation of materials with a variety of nanosize reinforcements (e.g. B_4C and Carbon nanotubes)
- Spray dried composite powder will be evaluated for enhancing the retention of the nanostructure.
- Process Optimization
- Measurement of thermal and mechanical properties at high temperature.
- Investigation of multilyered nanocomposites for solar shade application.
- Examination of post spraying treatment (heat treatment and laser consolidation), high temperature mechanical testing (tensile and creep) and evaluation of fatigue propereties.
- Program review, final report and recommendations for full-scale evaluation.