REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT DATE /TYPE	3. DATES COVERED *(From - To)*
09/01/05	**Grant**	**07/01/05-09/30/05**

4. TITLE AND SUBTITLE

Development of Metal/Ceramic Nanocomposite Powder and Consolidation to Bulk Nanocomposite Components with Retained Nanostructures
Effect of Plasma Spray Parameters in Nanostructure Retention in Bulk Composites

5a. CONTRACT NUMBER

5b. GRANT NUMBER
N00014-02-0591

5c. PROGRAM ELEMENT NUMBER
068342

6. AUTHOR(S)

Seal, Sudipta; Georgieva, Petya;
Rea, Keith; Viswanathan Venkatachalapathy

5d. PROJECT NUMBER
02PR11049-00

5e. TASK NUMBER
N/A

5f. WORK UNIT NUMBER
N/A

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

UCF Office of Research
12443 Research Pkwy, Suite 207
Orlando, FL 32826

8. PERFORMING ORGANIZATION REPORT NUMBER
9H673
8252AA

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Office of Naval Research
One Liberty Center
875 North Randolph Street, Suite 1425
Arlington, VA 22203-1995

10. SPONSOR/MONITOR'S ACRONYM(S)
ONR

11. SPONSORING/MONITORING AGENCY REPORT NUMBER

12. DISTRIBUTION AVAILABILITY STATEMENT

Free Form Bulk Nanocomposites

DISTRIBUTION STATEMENT A
Approved for Public Release
Distribution Unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT

This report summarizes the challenges for the optimization of the plasma spray parameters for manufacturing a dense ceramic nanocomposite. Various design parameters have been developed to achieve a high density bulk composite part. To prove the feasibility of the plasma spray toward nano-manufacturing of different shape and size parts, a large component with the ONR logo has been created with two dissimilar materials. The newly developed method named as plasma pen lithography (PPL), was shown useful for design of large scale bulk components. The microstructure of the as-designed parts was characterized using advanced SEM, FIB and TEM techniques to visualize the retained nanostructures in the composite.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF: a. REPORT	b. ABSTRACT	c. THIS PAGE	17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
			SAR		**Sudipta Seal**
					19b. TELEPONE NUMBER *(Include area code)* **(407) 882 1119**

Interim Report
Office of Naval Research
Young Investigator Program
Fiscal Year 2005

Development of Metal/Ceramic Nanocomposite Powder and Consolidation to Bulk Nanocomposite Components with Retained Nanostructures

Subtitle: Effect of plasma Spray Parameters in Nanostructure Retention in Bulk Composites

Contract Number: ONR YIP N00014-02-1-0591
DURIP N00014-03-1-0858

Submitted By

Sudipta Seal, Ph.D.

Advanced Materials Processing and Analysis Center (AMPAC), and
Mechanical, Materials, Aerospace Engineering
University of Central Florida
Eng I, Suite #381, 4000 Central Florida Blvd.,
Orlando, FL 32816.

Dr.A.K. Vasudevan

Program Manager
Scientific Officer, Materials Divisior

Content

Summary of Previous Report

- Spray drying temperature was found to have an influence on the density and the mechanical properties, such as hardness. It was confirmed by varying the spray drying parameters at select plasma spray condition.

- Influence of phase transformation of alumina from gamma to alpha phase has been studied. The alpha phase has a high packing factor compared to gamma alumina and leads to further densification.

- Hardness values increased three fold due to the presence of coherent interface formation as observed in bright field HRTEM images. Density improvement is caused by the increase in the packing efficiency of the unit cells of alumina, triggered by the phase transformation from gamma to alpha phase. Gradual elimination of porosity by decreasing the spray drying temperature was evident using SEM micrographs.

- Nanostructure retention after plasma spray processing has been ascertained using High Resolution TEM analysis.

- THE OBJECTIVE OF THE CURRENT REPORT

    - Design and Manufacture a bulk nanocomposite plate
    - Vary various plasma spray parameters to achieve high density
    - Cross Section TEM to prove the retention of nanostructures in the bulk plate

PLASMA SPRAY PROCESSING OF SPRAY DRIED GAMMA ALUMINA PARTICLES:

With established spray dried parameters, the plasma spray processing has been carried out with an effort to improve the density of the bulk plasma sprayed alumina. Four experiments were conducted with different primary and secondary gas flows, power ratings of the gun and stand off distance on 1" X 1.5 " mild steel coupons grit blasted with 60 grit size alumina for better deposition. The spray parameters are mentioned in Table I.

Table I Plasma spray processing variables

Sample	Voltage V	Current Amp	Standoff mm	Primary SCFH	Secondary SCFH	Powder wheel RPM	Carrier SCFH	Pass	Thickness		
									Initial, mm	Final, mm	Coating, μm
I	30	650	148	70	5	3	13	90	3.2	3.56	360
2	30	700	148	90	10	3	13	90	3.2	3.56	360
3	30	800	148	110	10	3	13	90	3.2	3.56	360
4	30	800	75	110	10	3	13	90	3.2	3.87	670

Scanning Electron Microscopy:

A Hitachi S3500 Scanning Electron Microscope operating at 30 kV was used in the study. The microstructure analysis revealed the importance of the plasma parameter-structure correlation.

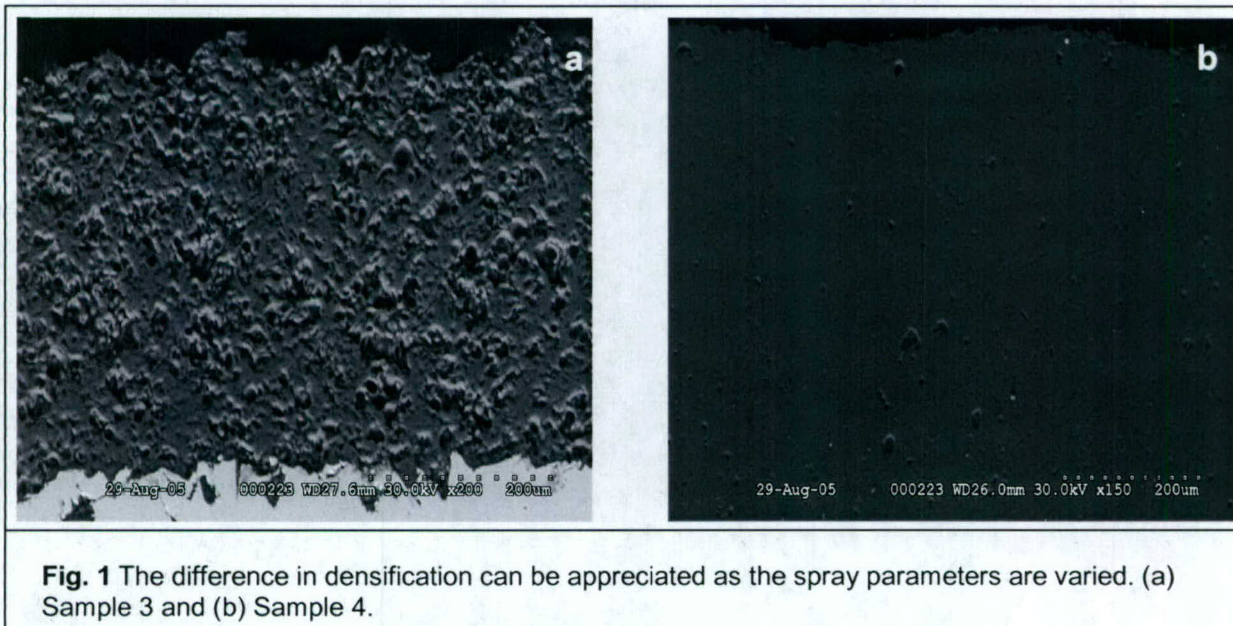

Fig. 1 The difference in densification can be appreciated as the spray parameters are varied. (a) Sample 3 and (b) Sample 4.

From Fig. 1, it can be concluded that the higher current, higher gas flow and closer standoff distance correspond to a denser coating. At the same time the lower coating porosity can be a sign of the improved fracture toughness, strength and the oxidation resistance of the coating. The denser coating (Fig. 1(b)) may be explained with the higher amount of explosion or "de-agglomeration" of the nanoalumina particles due to the higher gas flow and smaller particles' ability to fill the pores which agglomerated particles can not fill. These particles would have higher velocity and higher temperature as well. Hence, at impact with the substrate they will form much smaller lamellas, and more dense coating, which will consequently have a higher bond strength. If the standoff spray distance is smaller, the particles reach the substrate in higher states of temperature and velocity and form a more dense coating/bulk component.

Mechanical Aspects of Bulk Nanostructured Component Manufacturing:

The specific mechanical procedure for producing bulk components while maintaining the nanostructure and density requires a calculated standoff distance as described further in the parametric section and microstructurally visualized in the scanning electron microscopic images and TEM images displayed in Figures 1 and 7, respectively. To establish the deposition screen for creating the lettering as shown in figure 2, we specifically machined a template from mild steel with a high surface finish to resist coating and deposition with the inverse design of the deposition lettering as depicted in figure 2.

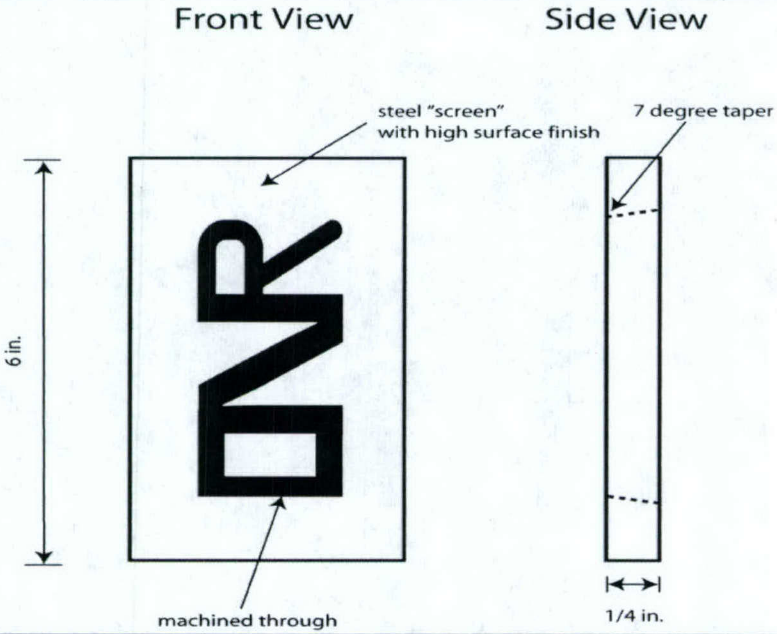

Fig. 2. Template made of mild steel with ONR logo machined

The screen was affixed to the substrate after deposition of a base coating of the spray-dried Al_2O_3 powder feedstock with a thickness of approximately 30-40 mm as shown in figure 3 prior to deposition of the TiO_2 lettering. The spraying parameters for optimal deposition were recorded and tabulated in Table 1 prior to the experimental procedures. With sufficient deposition in less than one hour, both the Al_2O_3 and the TiO_2 lettering were created using air plasma spray forming to fabricate a large nano-composite plate with two dissimilar materials. We name this process as plasma pen lithography (PPL) to fabricate bulk nanostructures.

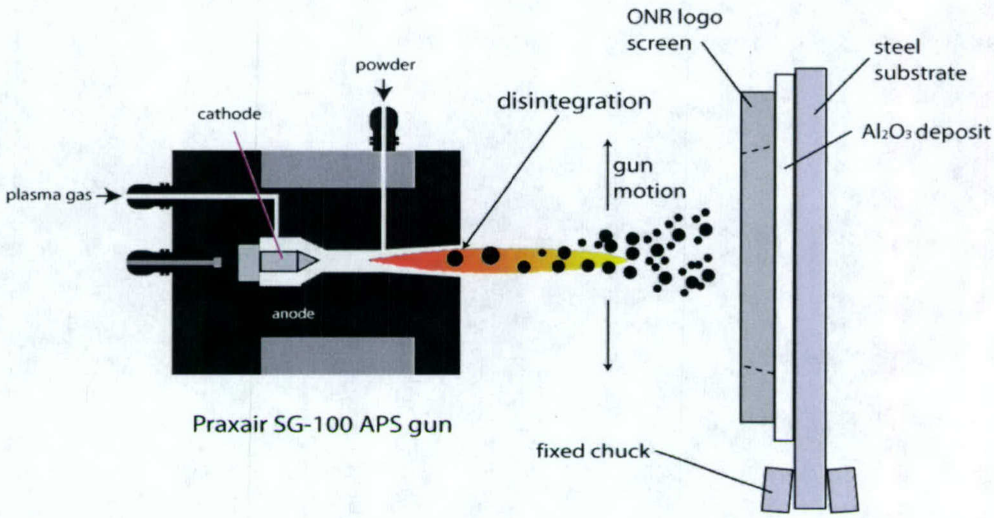

Fig. 3. The formation of alumina base coating followed by overlaying Titania lettering

The "ONR" logo prototype part was then mounted in Lucite (Admento Promotions, NY) with a distinguishing black colored descriptive background as shown in Figure 4 and 5. We further optimized the plasma spray parameters using the spray dried Al2O3 (130 C) powder to create a bulk component which will be characterized more extensively in further communications (listed as sample 4 in Table 1, and SEM cross-section image in Figure 1 (b).

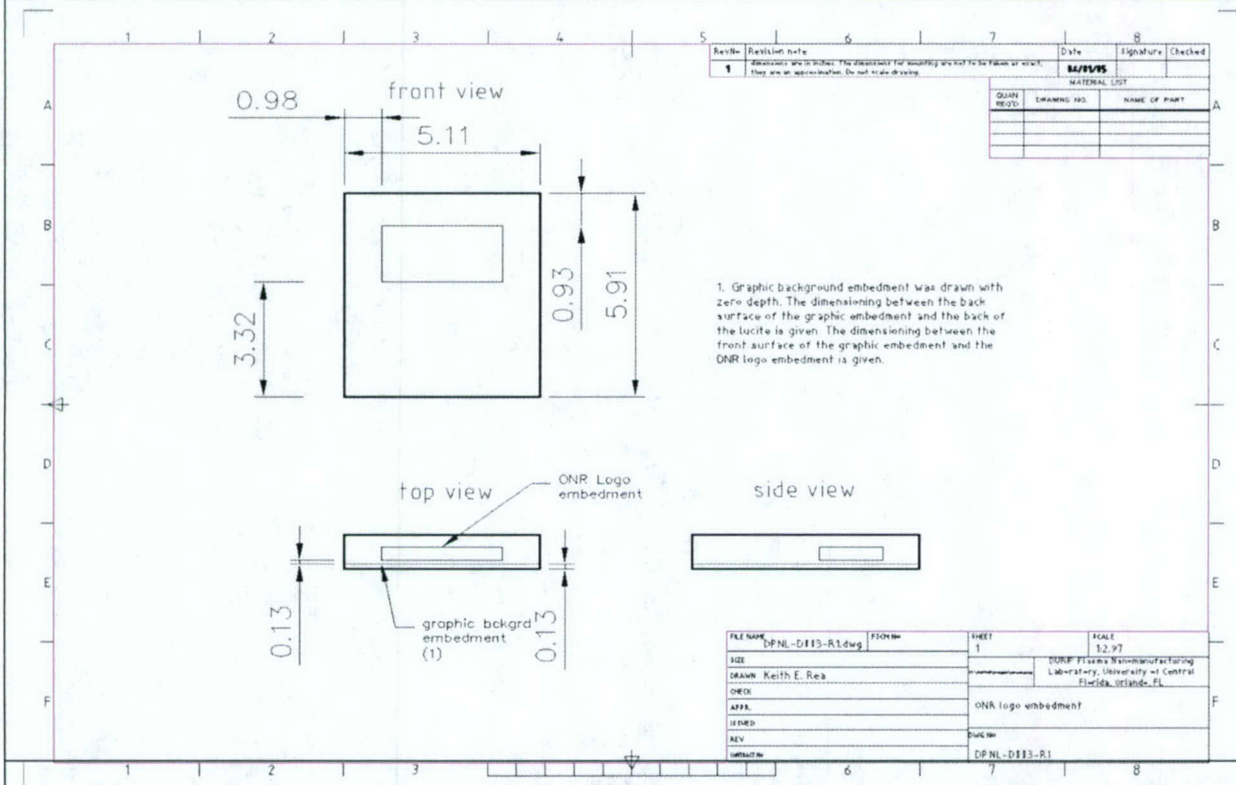

Fig. 4. The process of formation of base alumina coating followed Titania lettering

Fig. 5. Prototype Logo mounted in lucite.

Focused Ion Beam Sample Preparation for Transmission Electron Microscopic Nanostructure Analysis:

To study the nanostructure retention in the composite, a liftout procedure for preparing transmission electron microscopic samples was followed to prepare a cross-section sample of dimensions 20 μm length, < 150 nm thick, and 4 μm height to be analyzed in the TEM [1]. The sample was milled using an FEI 200 FIB TEM and final thinning mill patterns were performed at < 300 pA beam current to produce a cross-section sample with thickness < 1 μm for removal as shown in Figure 6a. The sample was placed on a specially prepared "holy" copper TEM grid as shown in Figure 6b. Once placed mechanically on the grid using the in-situ technique and the OmniProbe, the probe was milled from the sample and the final stages of thinning were performed at < 30 pA leaving a sample of thickness of less than 150 nm as shown in Figure 6c.

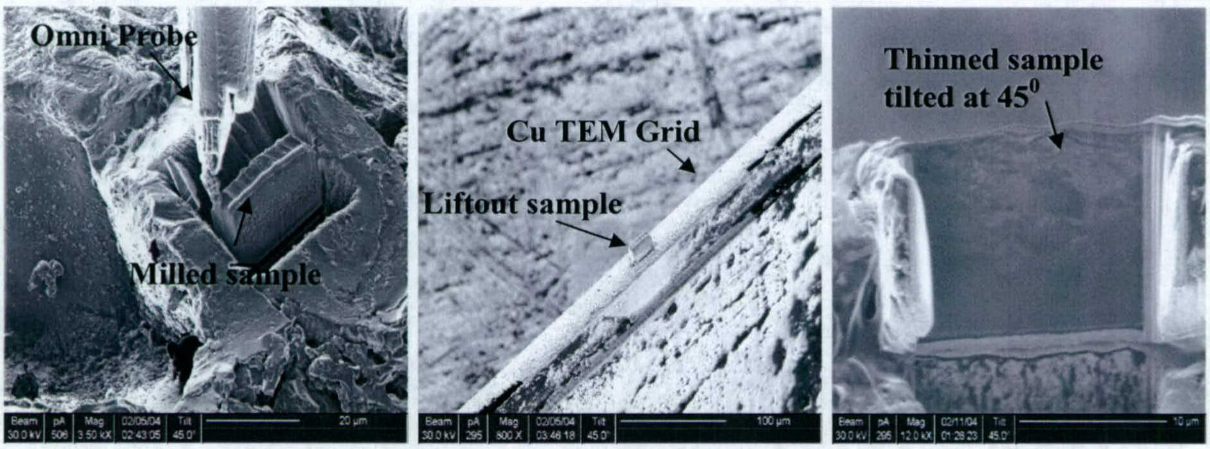

Fig. 6 (a) FIB Milled sample ready for pull out , (b) Sample resting on the Copper grid and (c) Thinned TEM sample at 45 ^{0} tilted position.

Revelation of Bulk Component Nanostructure using Transmission Electron Microscopy:

High-resolution transmission electron microscopy (HRTEM) were carried out, using a FEI Tecnai F30 at 300 *kV*, to investigate the size and structure of the nanoparticles. Specimen preparation for TEM and OIM studies was carried out on focused ion beam equipment.

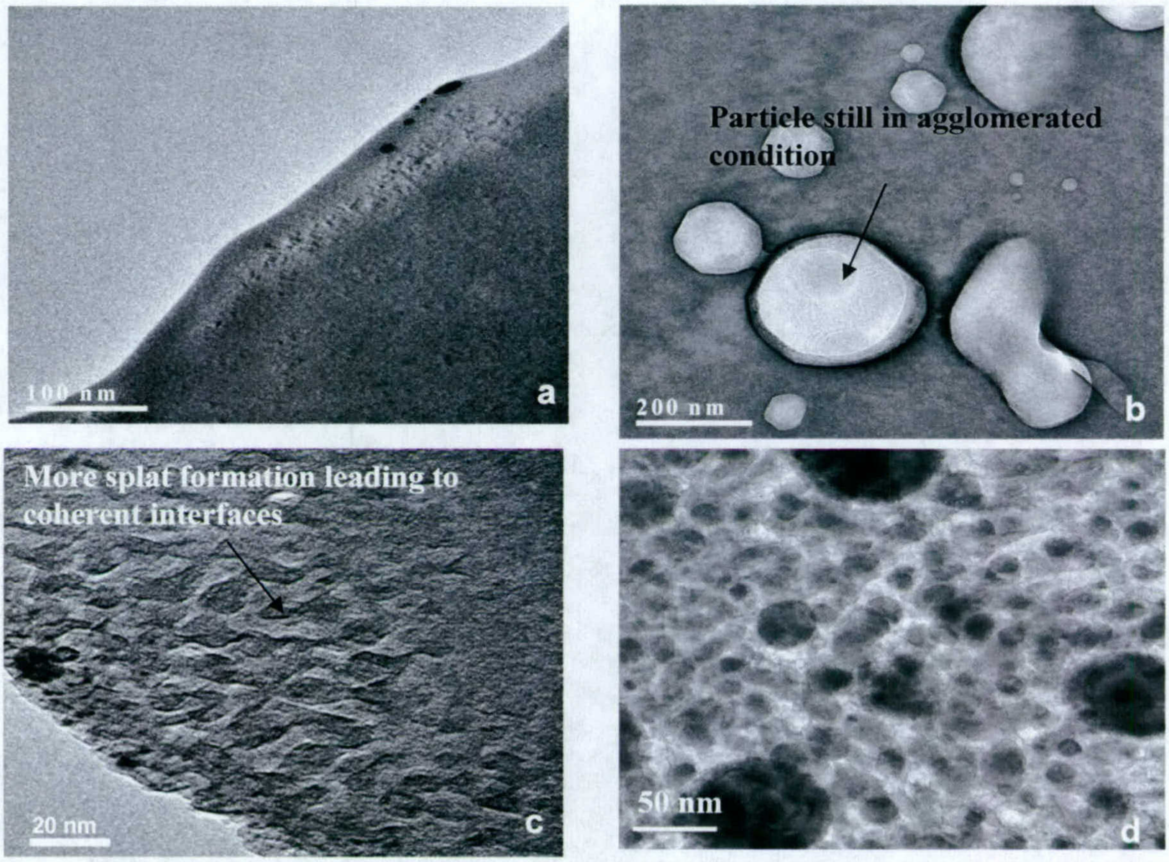

Fig.7 a,b,c Nanostructures corroborated using High Resolution Transmission Electron Microscopy sprayed from 130^0 C spray dried particles compared with (d) nanostructures from 210^0C spray dried alumina particles.

Fig. 7 (a) and (b) depicts a low magnification image of the nanostructures from a bulk nanocomposite. The concept of developing dense nanostructures seems hinged on to the proper control of spray drying parameters as well as the plasma spray parameters. From Fig. 7 (b), there are still some residual agglomerated particles that did not fall on the core of the plasma plume and did not get exploded well enough. However, with a slew of parameters that can be varied during plasma spray, there can be a complete de-agglomeration effect possible which will lead to dense nanostructures. As discussed in the last report, more and more coherent interfaces lead to improvement of mechanical properties such as Hardness. It is clear that the amount of coherent interface formed has increased (figures 7 c and 7 d) with the reduction in spray drying temperature. The plasma spray parameters for both the spray dried powders were retained the same in order to appreciate the differences in the microstructure. THUS WE ARE ABLE TO

FABRICATE FAIRLY LARGE NANOCOMPOSITE PLATES USING PLASMA SPRAY FORMING.

Participants

- Dr. Sudipta Seal, Associate Professor, AMPAC and MMAE, UCF.
- Petya Georgieva, Ph.D. student and Graduate Research Associate, AMPAC and MMAE, UCF.
- K. E. Rea, Masters Student and Graduate Research Assistant, AMPAC and MMAE, UCF.
- V. Viswanathan, Ph.D. student and Graduate Research Associate, AMPAC and MMAE, UCF.

References

- [1] K.E. Rea , A. Agarwal, T. McKechnie and S. Seal , FIB Cross Sectioning of a single Rapidly Solidified Hypereutectic Al-Si Powder Particle for HRTEM , Microscopy Research and Technique 66:10-16 (2005).