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14. ABSTRACT The objective of the research is to show that ceramic particles can be melted in flight, undercooled in flight, and impacted on a substrate to form a thick film. It is further hypothesized that with adequate process control, deposits of high temperature ceramics can be created on heat sensitive substrates, e.g., hybrid electronic structures. The approach is to flow powders in a gas stream through a region of high photon flux to melt the powders, cool the molten particles by radiation, convection and conduction during free flight, and control phase selection and droplet spreading on a substrate by modeling, in-process diagnostics, and metallographic examination of the deposits. The primary application of this process is for the sealing of hybrid ceramic bio-implantable devices, such as pacemakers. Ceramic pacemakers have communication capabilities, integrated feedthroughs, and are MRI and biologically compatible. There is presently no known biocompatible method for sealing these hybrid devices. Other applications include the formation of thick films at high rates for ceramic superconducting tapes and wires, ceramic superconducting coatings for electromagnetic shielding, thermal barrier coatings on heat sensitive substrates, micro coatings for MEMS components, and ceramic joining.

15. SUBJECT TERMS
undercooling, layered manufacturing, bio-materials, ceramics, superconductors, hybrid devices

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Final Report

Deposition of Undercooled Liquid Ceramics

March 24, 2001

Principal/co-Principal Investigator.

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* Number of refereed papers/book chapters to appear: 0
* Number of books published: 0

* Number of unrefereed reports and other articles: 0
* Number of project presentations: 0

* Number of patents granted and software copyrights: 0
* Number of patents filed but not yet granted: 0

* Number of graduate students supported >= 25% of full time: 0
* Number of post-docs supported >= 25% of full time: 0
* Number of minorities supported: 0

Summary of Objectives and Approach.

The objective of the research is to show that ceramic particles can be melted in flight, undercooled in flight, and impacted on a substrate to form a thick film. It is further hypothesized that with adequate process control, deposits of high temperature ceramics can be created on heat sensitive substrates, e.g., hybrid electronic structures.

The approach is to flow powders (individually or en masse) in a gas stream through a region of high photon flux (a laser beam) to melt the powders, cool the molten particles by radiation, convection and conduction during free flight, and control phase selection and droplet spreading on a substrate by modeling, in-process diagnostics, and metallographic examination of the deposits.

The primary application of this process is for the sealing of hybrid ceramic bio-implantable devices, such as pacemakers. Ceramic pacemakers have communication capabilities, integrated feedthroughs, and are MRI and biologically compatible. There is presently no known biocompatible method for sealing these hybrid devices. Other applications include the formation of thick films at high rates for ceramic superconducting tapes and wires, ceramic superconducting coatings for electromagnetic shielding, thermal barrier coatings on heat sensitive substrates, micro coatings for MEMS components, and ceramic joining.

Summary of Technical Progress.

A process simulation was developed, and experiments in heating and melting powders with various light sources were carried out. Powder delivery through a laminar flow nozzle was accomplished and the flow rates, particle velocities, and dispersion of the particle stream were measured. Samples from experiments with a 4kW laser diode source were examined in a scanning electron microscope. Apparatus was constructed to allow manipulation of the particle stream with a robot arm, and deposits of alumina and high temperature superconductors were produced.

A summary with pictures and movies is available in Power Point: "deposition of undercooled liquid ceramics final report.ppt" .

Powder heating - Heating sources such as a quartz lamp, nichrome wire, laser diodes, Nd:YAG laser, 4kW diode laser, and 3 kW CO_2 laser were examined. The former sources do not have enough fluence to melt alumina powders in flight, but are useful for preheating powder streams. Testing was accomplished with a Pt-Rh thermocouple placed in the powder heating area. The nichrome wire heater was deemed the best for heating up to 1000C where the powder stream is still contained in a quartz tube. Above this temperature powders tend to stick in the tube, and further heating must be done in the free (uncontained) stream. A 45 watt three bar diode laser was tested with diffuse reflectors of various diameters. The temperature reached by the thermocouple was inversely proportional to the area (diameter) of the reflector. Various lens/reflector combinations were tested with a 150W Nd:YAG laser as well. The Nd:YAG laser with a cylindrical lens and reflector was capable of melting stationary powders, however, the 4 kW source was necessary to melt moving particles in cold gas streams. Melting experiments using the 4 kW diode laser were carried out on powders from 45-109 microns in diameter, at 4kW and velocities up to 10 ms^{-1}. Four different powders were tested, two high purity grades of alumina, one low (96%) purity grade, and high temperature superconductors. The results of all the above experiments were used to tune the process simulation. In addition, similar powders were tested using a 3kW CO_2 laser at University of Tennessee Space Institute in Tullahoma, TN.

Nozzle testing - Because the energy absorbed by the sample in an optical beam is proportional to the residence time, it is important to propel particles at as low a velocity as possible for melting. The design trade-off is the velocity required to spread the droplet on a substrate. A one mm i.d. pipette was tested with powders from 50-70 microns in diameter at 20 ms^{-1}. At a 4 cm distance, less than 10% of the powder fell outside a 4 mm diameter. This design is considered sufficient for initial tests.

Deposits – It is evident from the 4 kW laser tests that a multi-stage heating apparatus is necessary to melt alumina at sufficient velocity to form good coatings. The deposits formed with the lower purity alumina were agglomerations of spheres, except where some portion of the optical beam was directed on the deposit. In these cases, monolithic deposits were created. The lower melting temperature and higher absorptivity of the ceramic superconductors allowed melting in the 4 kW beam and thick film deposits were generated. These experiment were repeated with the 3 kW CO_2 laser. This laser showed better absorptitivy, but had less total power. Results were similar.

Summary - The high temperature superconductors show good promise for thick film deposition. Higher temperature ceramics, such as alumina will require about twice the power in the optical beam, i.e. 8kW, for deposition to be successful.

Transitions and DOD Interactions.

Contacted Harold Weinstock AFRL/AFOSR concerning fabrication of superconducting films.
Contacted Don Gubser and M.A. Imam at NRL concerning superconducting deposits.

Current Students and Recent Graduates Supported by ONR.

1. Name: Blythe Gore
   + US Citizen/Permanent Resident: citizen
   + Thesis: none
   + Graduated: scheduled to graduate from Northwestern May, 2001
   + Home Page:
   + Job: Ms. Gore was employed as a summer undergraduate worker

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Related Research Projects.

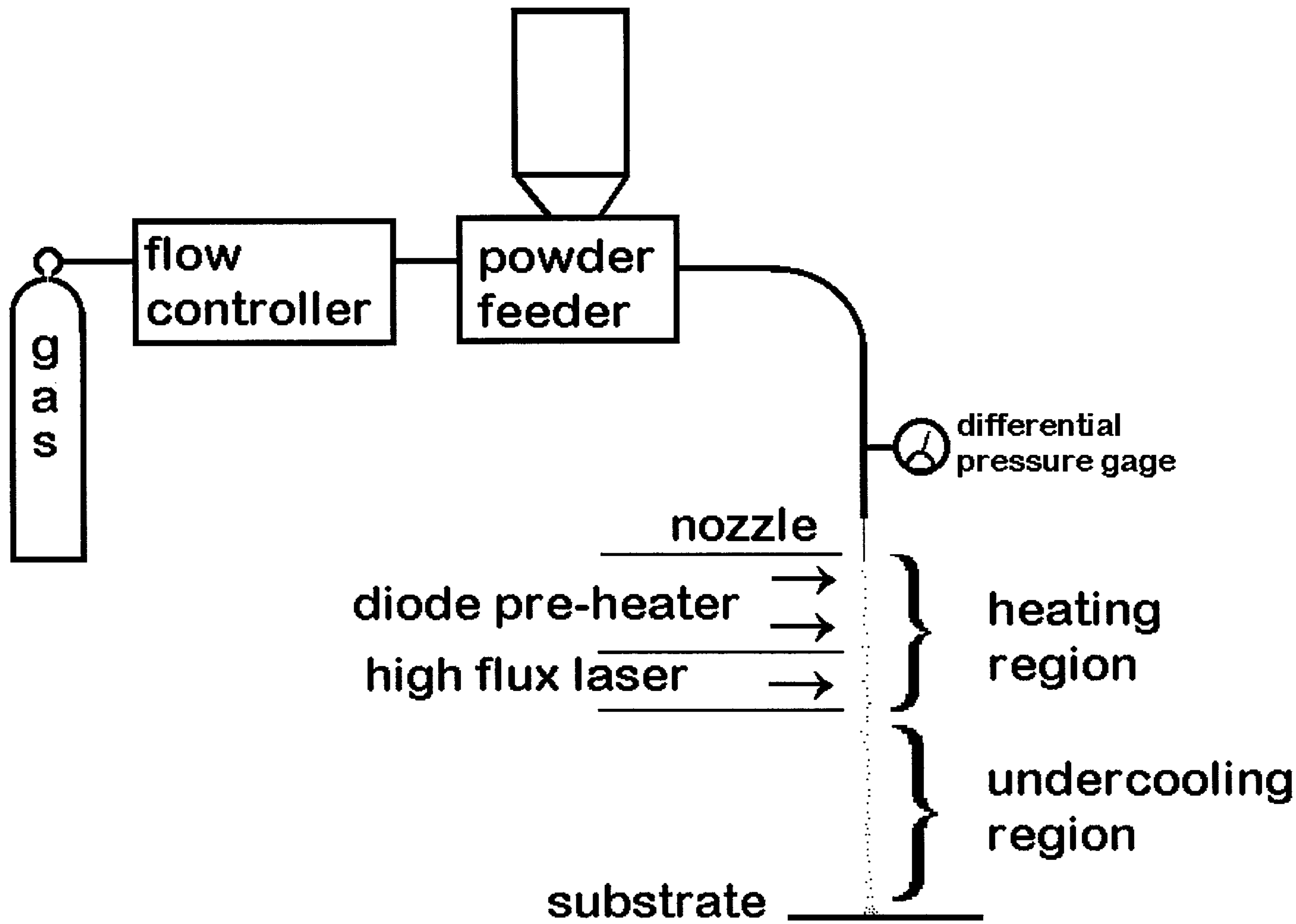
Microgravity Processing of Oxide Superconductors (NAG8-1275, end date May 31, 2000). This project is related because of the emphasis on controlling phase selection via undercooling and splat quenching.
High Speed Thermal Imaging for Process Development and Control (Sandia National Laboratory, contract BD-0123) is related because of the work with in-process thermal imaging and control of laser processes.
Superconductor deposits on textured substrates were sent to Amit Goyal at Oak Ridge National Laboratories for texture analysis in conjunction with the RABITS program.

deposition of undercooled liquid ceramics

William Hofmeister
Department of Chemical Engineering
Joseph Wehrmeyer
Department of Mechanical Engineering
Vanderbilt University

ONR grant number N00014-00-1-0442

Schematic of ceramic deposition technique



Advantages of Undercooled Liquid Ceramics

- Undercooling gives some control of phase selection
  - Peritectic materials
  - *In situ* nanostructures
- Viscosity increase aids droplet spreading
- Deposit on heat sensitive substrates
- Texture possible

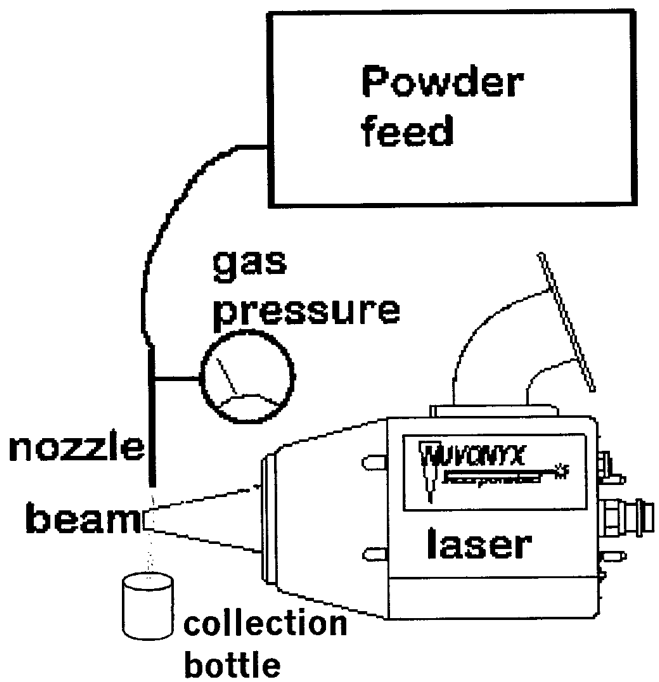
comparison with other free form ceramic deposition techniques

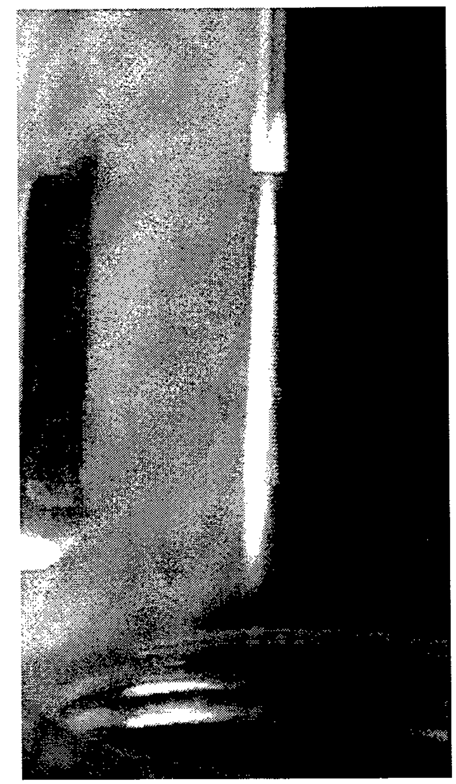
	Undercooled Liquids
• 3D printing/ Robocasting slurries	
– Require heat treatment	used as-deposited
– Polycrystalline	possible texture/epitaxy
• Selective Laser Sintering	
– Porous structures	solidification to full density
• SALD	
– Vapor decomposition is slow	$>10^3$ faster deposition
– Features controlled by beam size	features controlled by powder size

Applications of Undercooled Liquid Ceramics

- Hermetic sealing of ceramic enclosures for implantable devices (Medtronic, Inc.)
  - Pacing and neurological devices
  - Bio-inert, MRI compatible, integrated feedthroughs, telemetry
- Thick films of high temperature superconductors
- Free-form fabrication of insulators
- Ceramic welding
- Thermal barrier coatings

Powder melting experiments

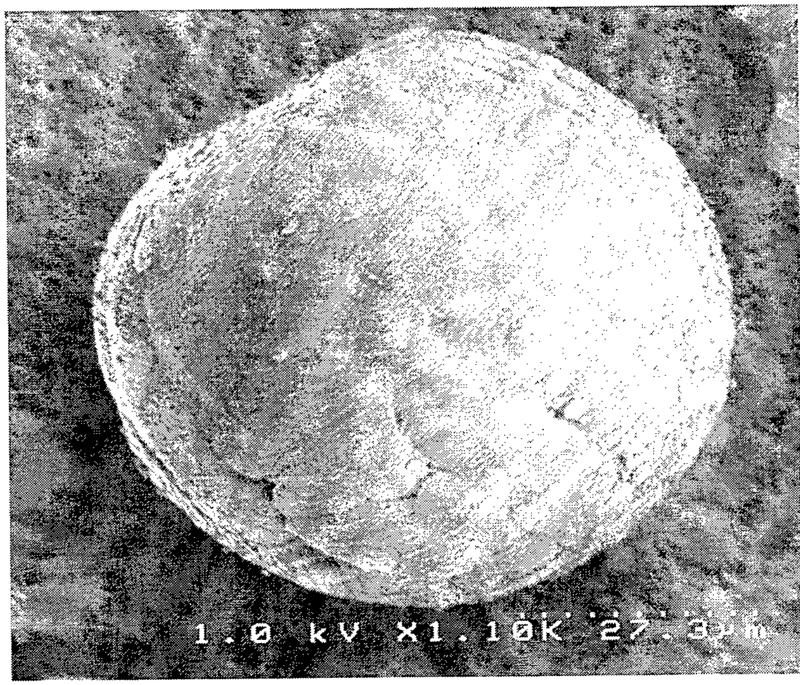


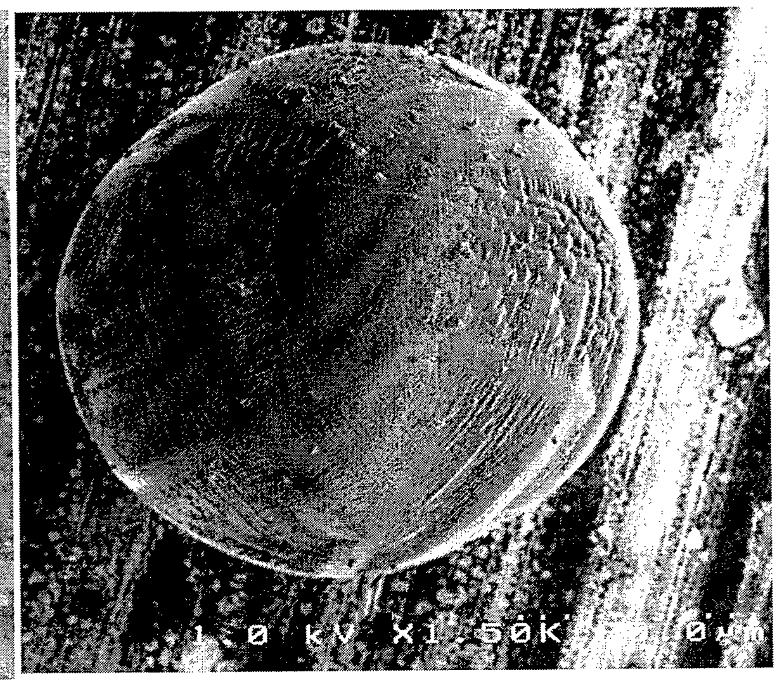


Click picture to run movie

Powders were collected as a function of particle velocity to determine residence time necessary for melting.

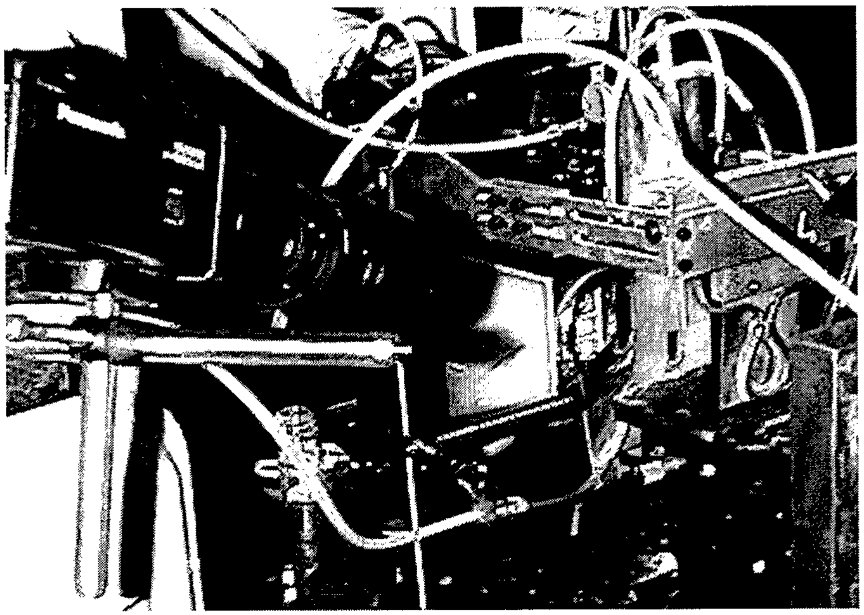
Microstructure of melted alumina





Melted particles are evident by the spherical shape and dendritic or faceted/dendritic structures. (velocity = $5ms^{-1}$, power = 4kW)

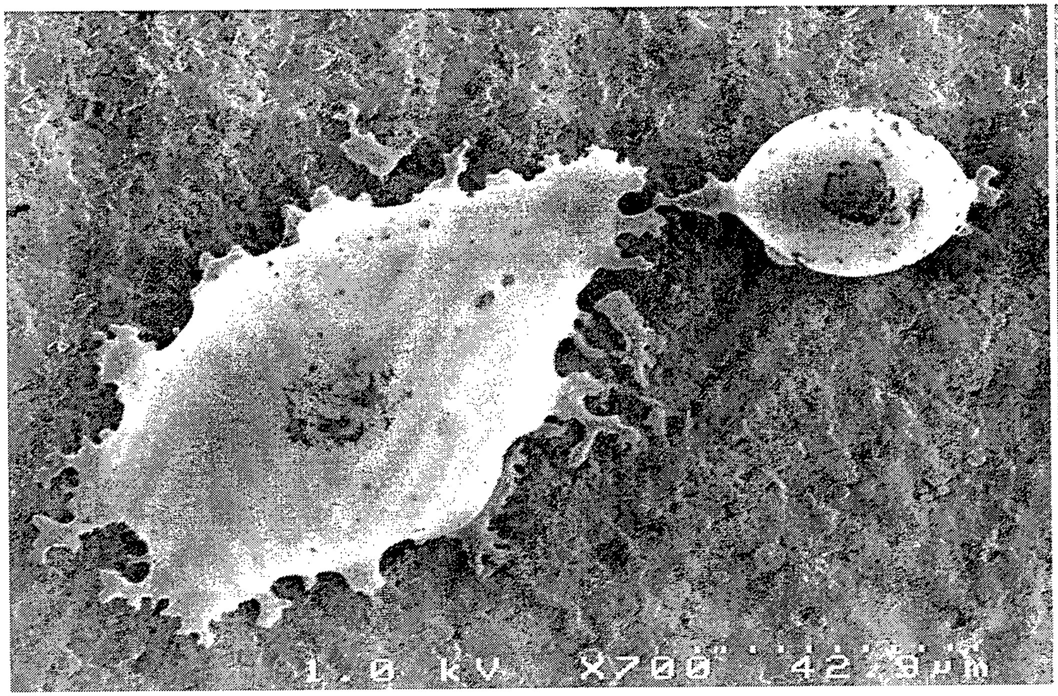
Substrate deposition

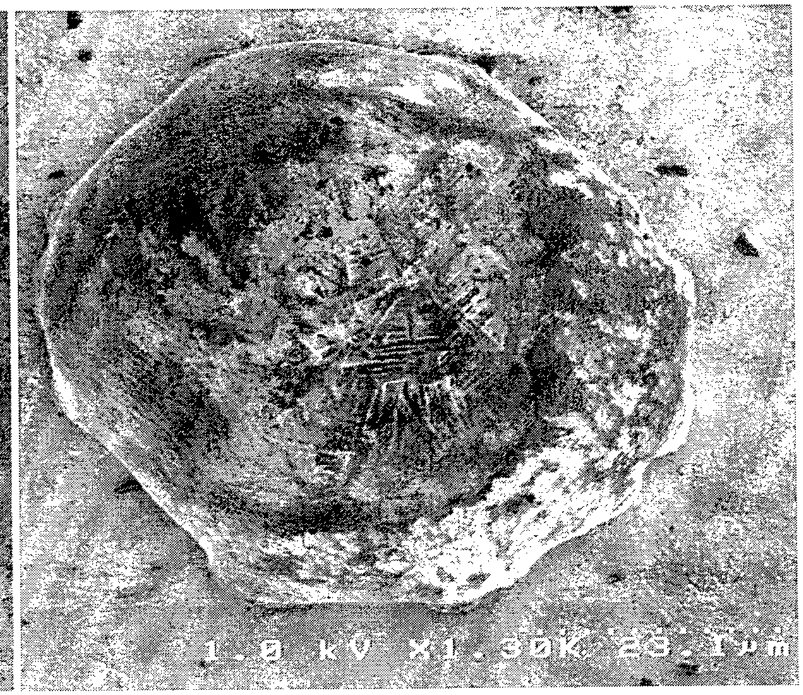


Click picture to run movie

The Nuvonyx 4kW diode laser is shown mounted to a robot arm. The robot was used to manipulate the laser and deposition stream as shown in the movie.

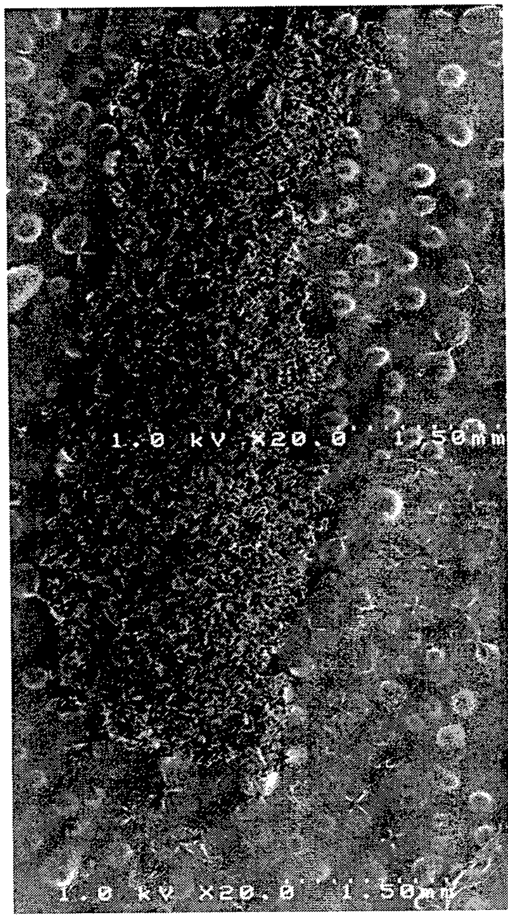
Splats on substrates



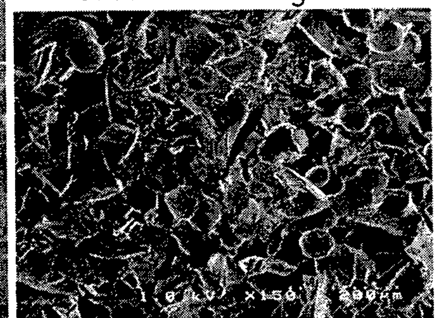


These alumina particles were impacted on a high purity alumina substrate at a velocity of 5 ms^{-1}. The velocity is too low for adequate spreading of droplets. The 4kW source alone is insufficient to melt alumina at higher velocities.

Alumina line builds

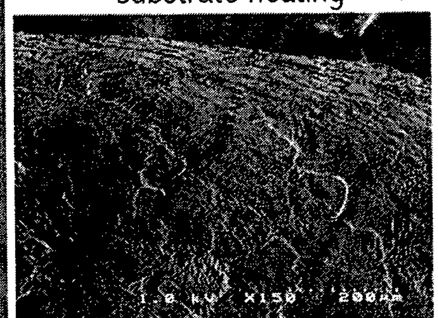


← Alumina deposit without substrate heating



surface picture of left deposit

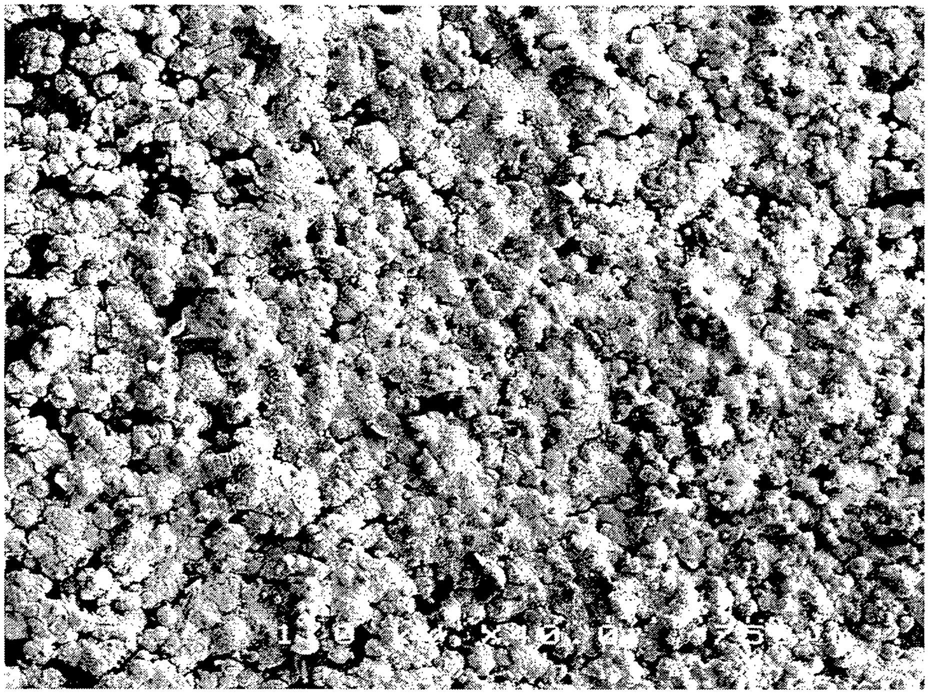
Alumina deposit with substrate heating →



surface picture of right deposit

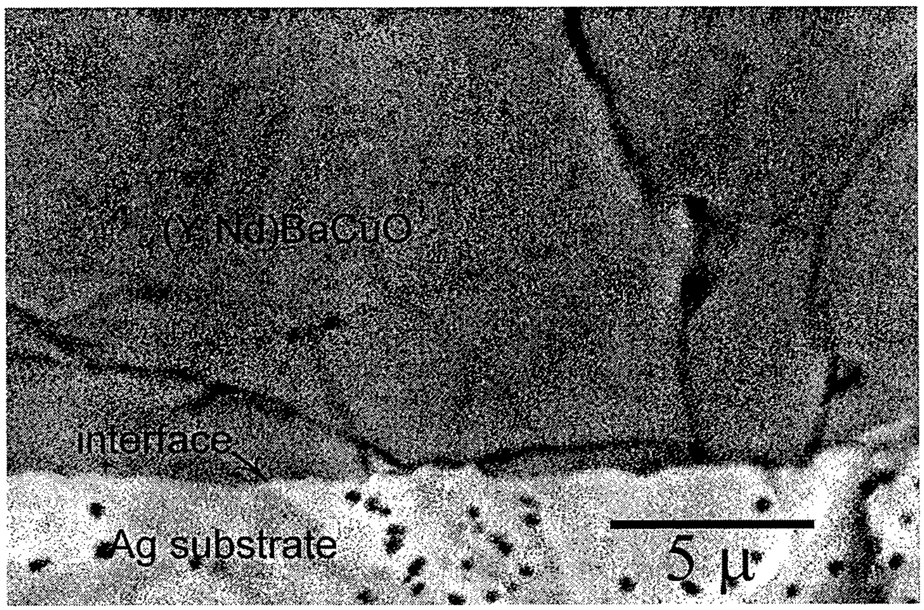
The alumina line deposit on the left was shielded from the beam and shows that the particle stream contains un-melted particles. The deposit is a loose aggregate of melted spheres and un-melted particles. The right deposit was exposed to a low energy portion of the laser beam so that impacting particles are melted on the surface for a smooth finish. (4 kW, 5 ms^{-1})

high temperature superconductor layer deposition

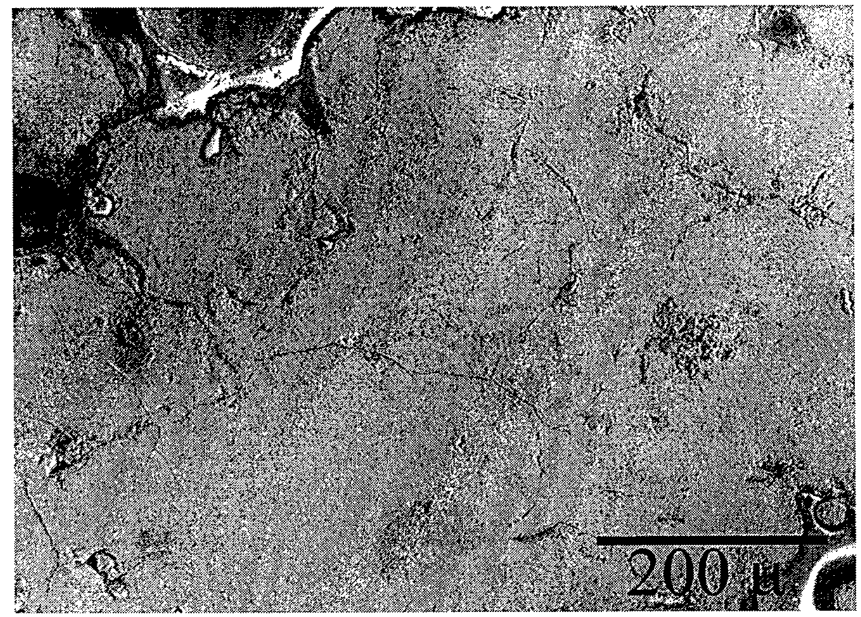


The high temperature superconductor $Y_{0.3}Nd_{0.7}Ba_2Cu_3O_{7-x}$ has a lower melting temperature and better absorptivity than alumina. The left deposit was 2mm below the laser beam, the right was 8 mm below. The velocities were 7 ms^{-1} and 9 ms^{-1}, respectively.

Microstructures of HTS deposits

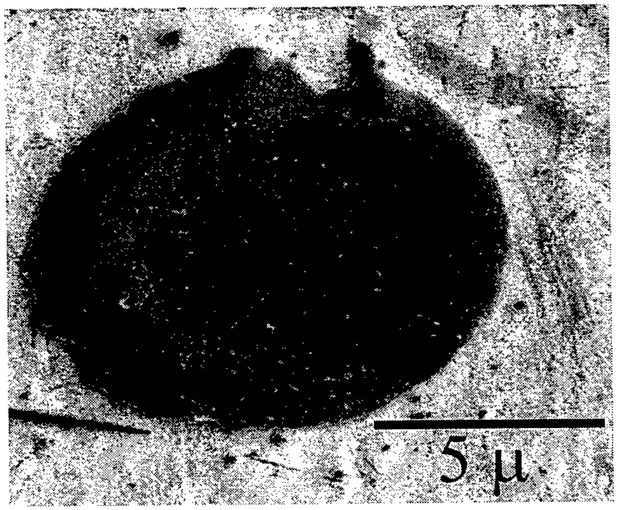


This cross-section shows a superconductor deposit on a polycrystalline silver substrate. The deposit is single phase, tetragonal 123.



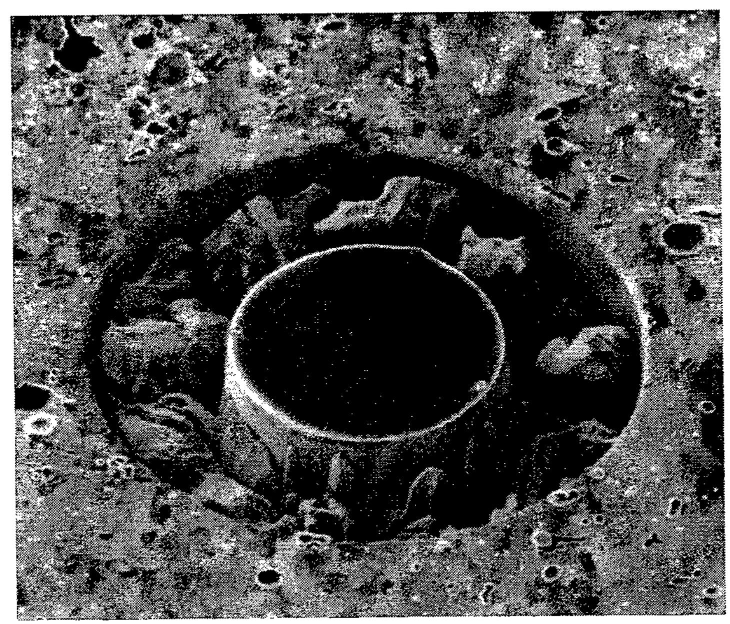
This is a section from a monolythic superconductor deposit 4 cm x 1 cm x 0.5 cm. The deposit is mostly 123 phase with some BaCu oxides.

Micron sized deposits

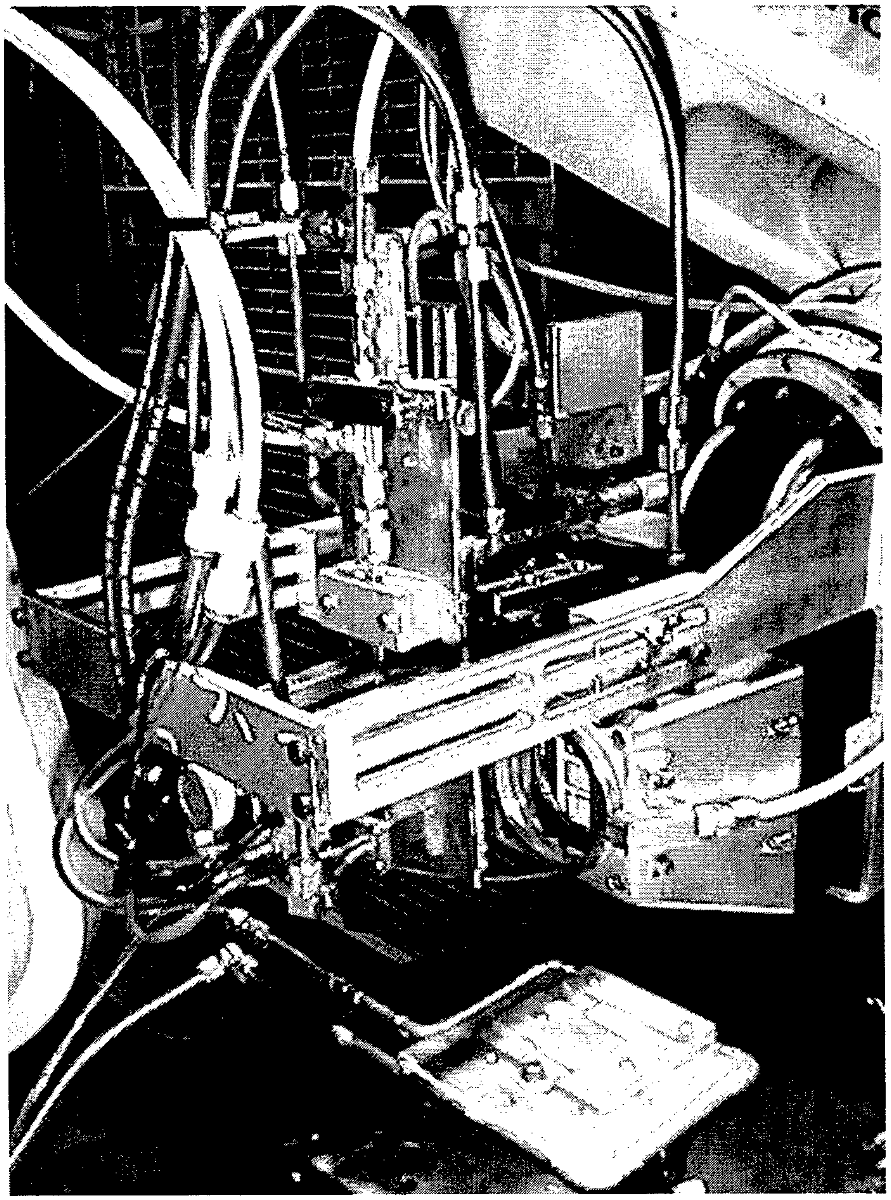


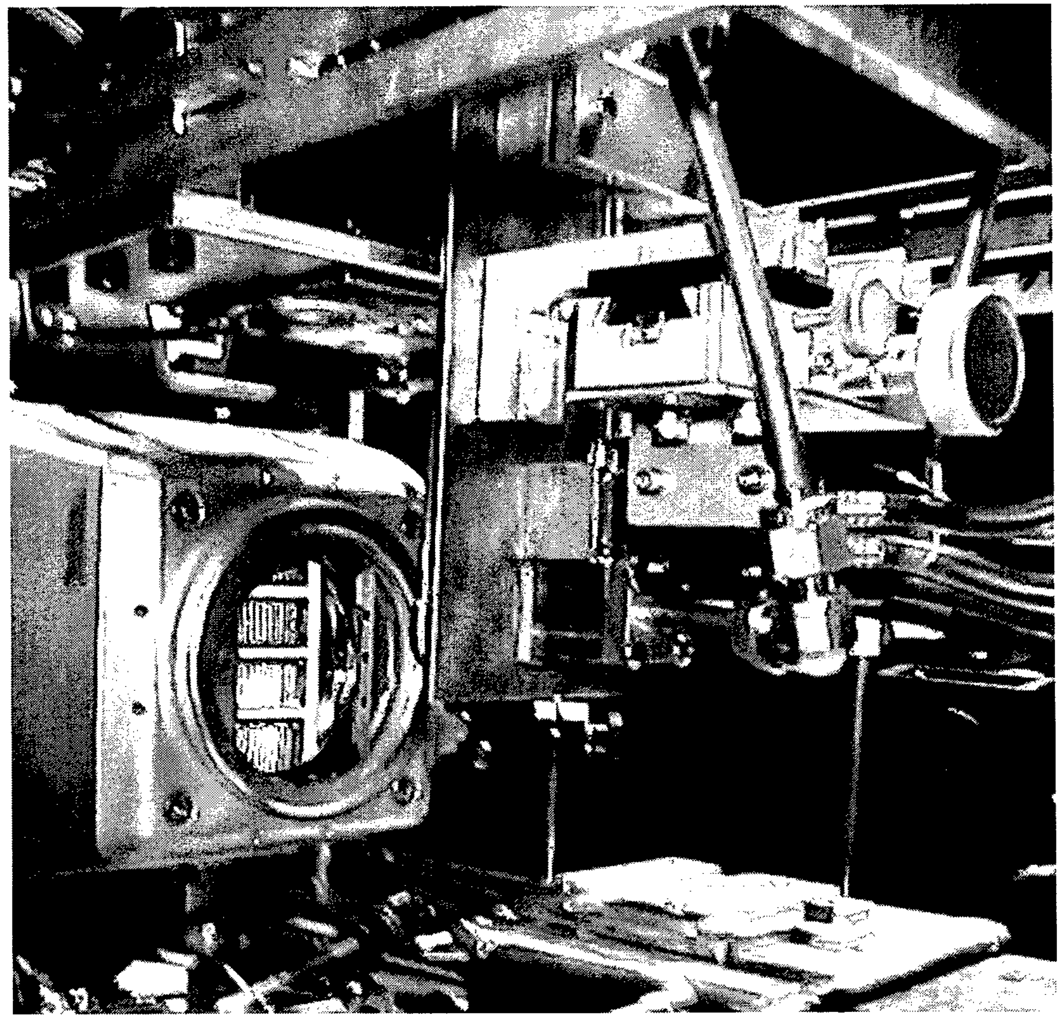
A pulsed eximer laser was used to melt particles and propel the liquid to a substrate. On the left is a superconductor splat from these experiments, on the right is an alumina splat.

A superconductor splat on a polycrystalline substrate was placed in the finely focused ion beam apparatus and trimmed to a 5 micron disk as shown on the right.



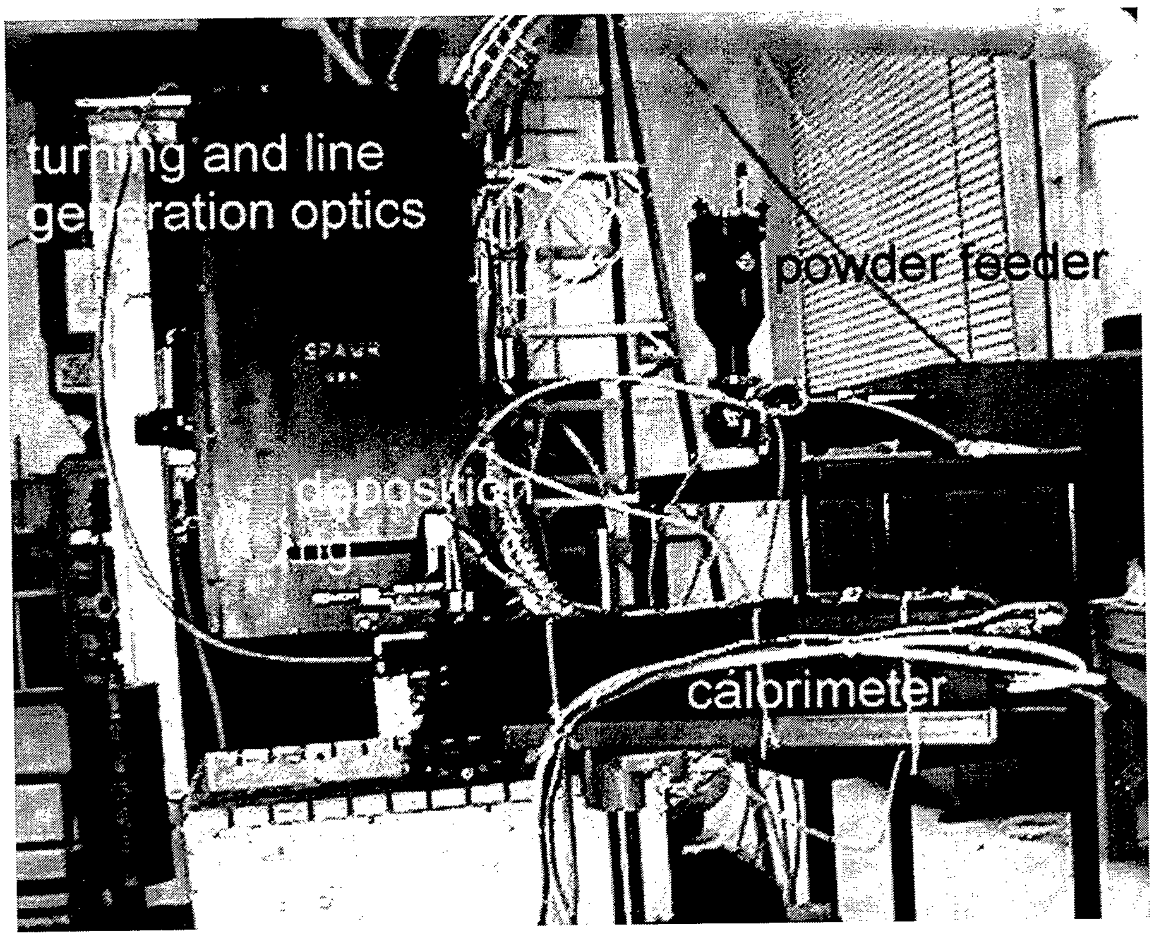
Diode preheat experiments

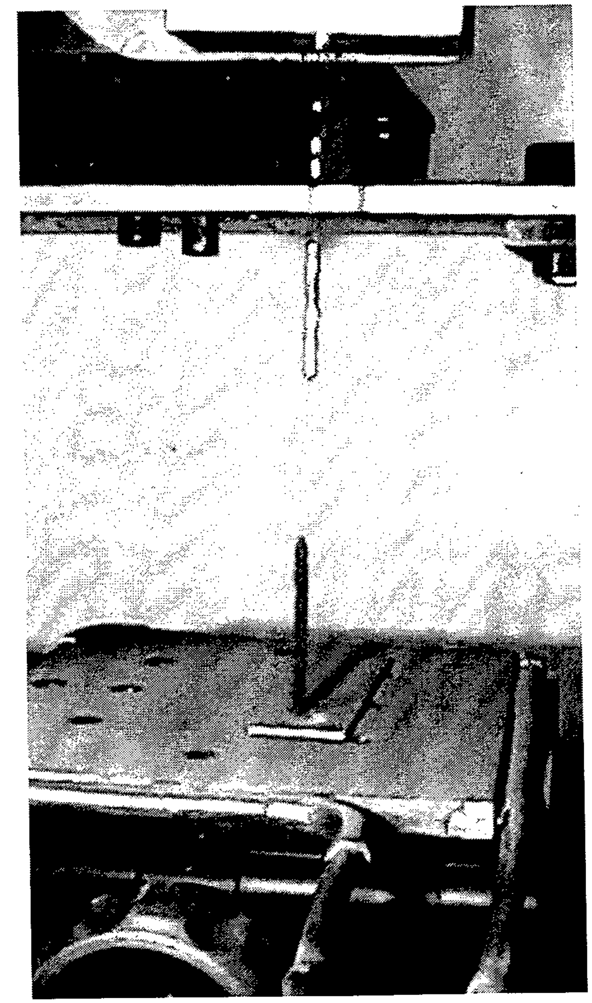




Diode preheat and reflector on main
Laser beam. Nuvonyx exps. Nov. 2000

Experiments at UTSI





UTSI CO_2 laser measured output was 2300 W. A sintered needle of alumina was built by indexing the laser in the z direction.

Alumina weld from UTSI

Click on picture to view movie

Alumina powders were melted in flight and the substrate rastered to form a weld on the alumina substrates. The deposit was a collection of sintered spheres and not 100% dense.

Tasks accomplished

- Powders
  - Various Al_2O_3, 96%-100%, coated and uncoated
  - Mullite
  - High Temperature Superconductors (Y-Nd 123)
- Nozzles
  - Laminar flow and co-flow
  - Measured velocity and divergence by collection and imaging
- Image furnace calculation strategy
- Models and Simulations
  - Newtonian simulator
  - Need to consider gradients, $\alpha(T)$, particle stream density
- Melting experiments
  - 810 nm Nuvonyx diode source
  - CO_2 laser at UTSI
  - Pulsed eximer laser

summary

- Melting and deposition of a stream of ceramic powders is feasible. High temperature refractories will require more than 4 kW of power for good deposits.
- Considerable scientific and engineering challenges remain on the path to a viable process.