Novel Process and Apparatus Design for Metalorganic Chemical Vapor Deposition (MOCVD) of Superconducting Thin Films

by

Brian Norio Hubert

Submitted to the Department of Mechanical Engineering
in Partial Fulfillment of the Requirements for the Degrees of
Bachelor of Science in Mechanical Engineering and
Master of Science in Mechanical Engineering at the
Massachusetts Institute of Technology

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Signature of the Author . . . .
Department of Mechanical Engineering
ay 10, 1996

Certified by .....
John Vander Sande
Associate Dean, School of Engineering

Certified by .....
Adjunct Professor of Mechanical Engineering

Accepted by.....
Ain A. Sonin
Chairman, Department Graduate Committee

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Abstract

In this work, a number of $YBa_2Cu_3O_{x-7}$ (YBCO) superconductor deposition systems developed by various laboratories are subjected to a critical review and analysis. Deficiencies in the design of these deposition processes, and deficiencies in the design of the mechanisms and tools used to carry out these processes are identified. Most of these deficiencies have resulted in either poor end-product performance or unlikely commercial viability. For example: pulsed laser deposition systems are capable of producing very high quality YBCO superconducting films, but their deposition rates are too slow to be commercially viable; liquid-source MOCVD systems can be precisely controlled, but the solvents they require tend to kill superconducting oxides; and solid-source MOCVD systems suffer from imprecise process control, thermal degradation of precursor materials, or both. A simple and affordable MOCVD system, called ConBrio, is proposed as an alternative to existing deposition systems.

Thesis Supervisor: John Vander Sande
Title: Associate Dean, School of Engineering

for

Mom

Dad

Kevin

special thanks

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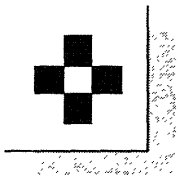

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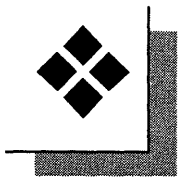

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1 Introduction

In 1911 scientists discovered that mercury becomes a superconductor at approximately 4 Kelvin. Over the next seven decades materials with higher superconducting transition temperatures were discovered and were eventually used to build low-temperature superconducting magnets and other highly specialized products. Unfortunately, the high cost of liquid helium coolant needed for superconducting operation was prohibitive in all but the most generously funded scientific and commercial endeavors. It was not until 1987 that researchers created a material with a transition temperature (T_c) above the boiling point of liquid nitrogen (-320 °F, or 77 K). The discovery of "high-temperature" (high-T_c) superconductivity was a momentous occasion because liquid nitrogen coolant is cheaper than milk. The dream of commercially-viable superconductors appeared to be at hand. Scientists, politicians, and eager investors had visions of superconducting transmission lines, levitated rail transit, ultra-efficient industrial motors, and magnetohydrodynamic propulsion systems for ships and submarines. By July of 1988, Congress was infused with superconductivity fever and rushed to establish research and development pilot centers at Argonne, Los Alamos, and Oak Ridge national laboratories. However, it was soon discovered that producing long lengths of wires from high-T_c materials would prove to be a daunting task, and over the next eight years advances in the field were slow but steady.

At last, in the spring of 1995, a small team of scientists at the Los Alamos National Laboratory announced a breakthrough that may push superconducting materials into the realm of practicality. The LANL scientists have revealed a superconducting tape that can carry 1.3 million amperes per square centimeter, about 1,600 times the current density of No. 12 copper wire, and is flexible enough to be wound into tight coils for magnets and other applications. In addition, the material can withstand applied magnetic fields up to 9 tesla at 75 K and exhibits superior flux pinning characteristics. The three-layer superconducting tape consists of $YBa_2Cu_3O_{x-7}$ (YBCO) thick film on a nickel-based alloy with a textured yttria-stabilized zirconia (YSZ) buffer layer.[1] Tape

construction begins with an ion-beam assisted deposition (IBAD) of zirconia --- the material used in imitation-diamond jewelry --- onto a nickel alloy substrate. The process requires two ion beams. One beam lays down minute layers of zirconia while a second beam *retards* the growth of misaligned zirconia crystals. The sophisticated process creates a highly textured zirconia surface that forces the correct alignment of subsequently deposited layers of YBCO. (YBCO's large-scale superconducting properties depend on nearly perfect alignment of its grains.) The YSZ also acts as a buffer layer that protects the YBCO from the detrimental surface effects of migrating nickel atoms. Finally, a layer of YBCO superconductor is applied to the tape using a pulsed laser deposition (PLD) technique. A pulsed laser vaporizes YBCO material off of a target and transports it in a plume to the zirconia-coated tape.

The LANL tape offers tremendous potential, and its electrical and mechanical performance is unparalleled. But the enthusiasm of commercial interests is limited by the fact that the protocol for producing the superconductor is excruciatingly slow and expensive. Greg Yurek, president of American Superconductor Corporation, has observed, "...it's going to take a while -- probably years, in fact -- to overcome the hurdles involved in terms of (turning the method) into volume manufacturing that can be done at a cost low enough to compete with other wire technologies". Commercial realizations of the LANL process may require multiple high power lasers that could cost millions of dollars a piece, and deposition rates are expected to continue to be very slow. These slow deposition rates --- which are usually measured in micrometers of film thickness deposited per hour (μm/h) --- are the Achilles heal for the LANL process primarily because practical applications of high-T_c materials will require thin tapes and wires many hundreds of meters in length. Commercially-viable production of such long tapes and wires can only be supported by deposition systems that are inexpensive to manufacture and maintain, have relatively few process control variables, are capable of high deposition rates, and can satisfy very long continuous-process runs. Production of superconducting wafers adds the additional need for large area deposition capability. In short, to be economically competitive, the processes for the deposition of both YSZ and YBCO layers must be dramatically accelerated and simplified without sacrificing product quality. Although the YSZ and YBCO layers are in direct contact with each other in the final product, the problems associated with their depositions can largely be addressed independently.

The author has chosen to focus his research efforts toward solving the problems associated with improving the performance and commercial viability of a YBCO layer deposition process. This paper provides a critical review of YBCO deposition processes currently available or under development at various research laboratories around the world. Deficiencies in the design of these deposition processes, and deficiencies in the design of the tools used to carry out these processes are highlighted. A novel YBCO deposition process is proposed and justified. Construction of a fully functional prototype deposition system is documented, and detailed design drawings are revealed. This work was carried out at the Los Alamos National Laboratory during the summer and fall months of 1995 under the direction of Dr. Xin Di Wu of the Superconductivity Technology Center, with the supervision of Dean John Vander Sande of M.I.T.

1. X. D. Wu *et al.* Submitted to Appl. Phys. Letters, 1995.

2 YBCO superconductor deposition systems

At the present time, the deposition of YBCO superconductor precursor materials onto a substrate can only be achieved by physical vapor deposition (PVD) and chemical vapor deposition (CVD). As discussed in the Introduction, PVD processes like pulsed laser deposition are slow and expensive, and commercial entities are reluctant to embrace the technology. Within the next 5 years it is likely that PVD deposition rates will be increased by an order of magnitude, but these rates will still be too slow -- and therefore too expensive -- for all but the most esoteric and specialized applications. On the other hand, good implementations of CVD processes benefit from the advantages of higher product throughput, low equipment costs, simpler and more robust operation, and capability for coating multiple, irregularly shaped substrates. In addition, CVD processes developed in the laboratory are relatively easy to scale up to manufacturing volumes.

Typical precursor materials for the formation of YBCO superconducting films by CVD processes have been metalorganic (MO) complexes of Y, Ba, and Cu. However, these reagents have very low vapor pressures that increase with increasing temperature, but thermally induced decomposition becomes significant, especially for the barium metalorganic precursors.[1] It is for these reasons that current YBCO MOCVD systems have their own subset of very significant problems including excessive residence time for precursor materials at degradation temperatures, lack of precise control over precursor delivery, and inconsistencies in product quality. But the *main* disadvantage of CVD stems from the difficulty of reproducibly transporting the metalorganic precursors to the substrate.[2] Nearly all YBCO MOCVD systems that have been developed by

1. W. J. Lackey *et al.* Appl Phys. Letters, Vol. 56, No. 12, 1990.

various laboratories and research institutions differ from one another primarily by their methods of precursor material delivery. Naturally, there are a host of other factors that have determined the relative success or failure of any of these systems, but many researchers in the field have come to recognize that optimal precursor material delivery is the key to successful YBCO superconductor formation. Currently, MOCVD systems offer at least four kinds of precursor delivery techniques: (1) liquid-source delivery with or without aerosol assistance and plasma enhancement, (2) free-flowing powder delivery, (3) bubbler delivery with or without carrier gas, and (4) solid-source delivery.

2.1 Liquid-source MOCVD

$YBa_2Cu_3O_{x-7}$ superconducting thin and thick films on $SrTiO_3$ substrates have been prepared by S. Matsuno *et al.*[1] using a single solution liquid-source MOCVD technique (Fig. 2.1). A tetrahydrofuran (THF) solution of Y, Ba, and Cu β-diketonate chelates (Y:Ba:Cu = 1:2.9:2.7)

2. J. Zhang *et al.* Appl. Phys. Letters, Vol. 61, No. 24, 1992.

1. S. Matsuno *et al.* Appl. Phys. Letters, Vol. 60, No. 19, 1992.

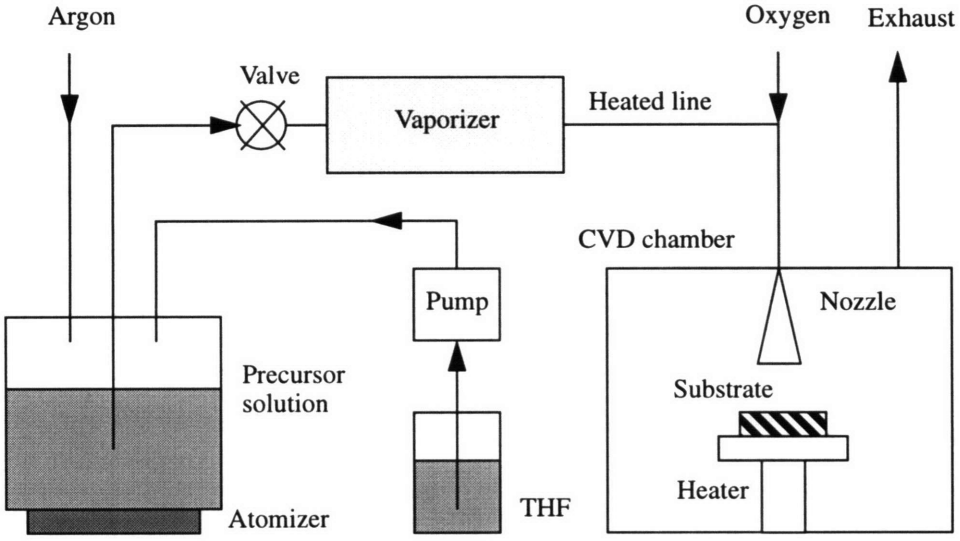

Fig. 2.1. Schematic of single solution liquid-source MOCVD apparatus. S. Matsuno *et al.*

is first atomized, then thermally vaporized at 230 °C, and finally deposited onto a 700 °C $SrTiO_3$ substrate within a cold wall, low pressure (10 Torr) CVD chamber. Solution feed control is regulated by applied power to the atomizer and argon carrier gas flow rate. Micropump injections of additional THF are needed to counteract excess source solution vaporization. After deposition, the films are cooled to room temperature under an oxygen pressure of 1 atm. The process has been used to produce 3.5 μm thick films at high deposition rates of 8 to 14 μm/hour. Critical transition temperature (T_c) and critical current density (J_c) were 91 K and 3.1 x 10^5 A/cm^2 (77 K) respectively.

This liquid-source technique offers satisfactory deposition rates and simple control of mass flow into the CVD chamber. Unfortunately, film critical current densities are rather low, and success of the technique is dependent on the choice of a suitably volatile precursor-compatible solvent. Throughout the deposition process, THF and β-diketonate concentrations in the solution reservoir are constantly changing due to excessive solvent evaporation, and there is an inherent time lag between the detection of concentration errors in the reservoir and rectification of these errors. Commercial realizations of this process can be large, complicated, and expensive. Advanced Technology Materials, Inc. of Connecticut manufactures several liquid delivery systems that retail between $100k and $250k.

At the very least, two variants on the liquid-source MOCVD technique are worthy of mention. Continuous depositions onto moving, elongated substrates (Fig. 2.2) are reported by

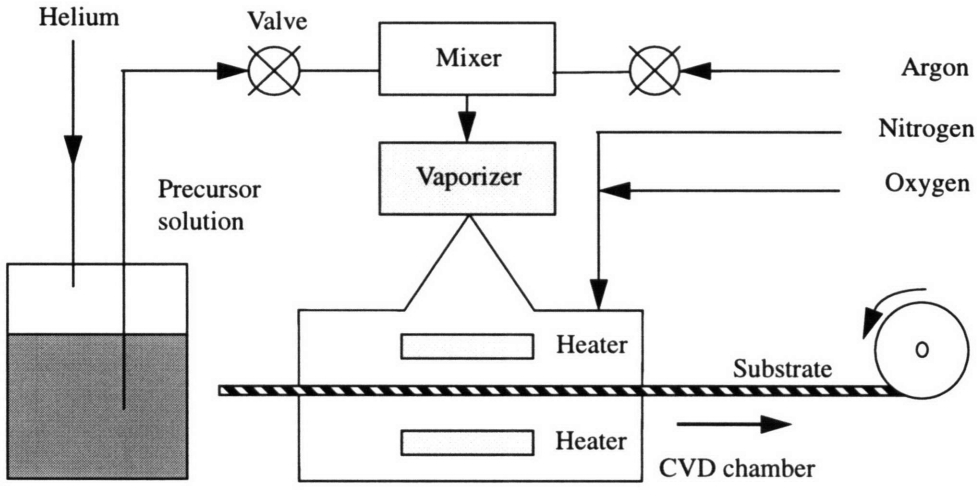

Fig. 2.2. Schematic of continuous process liquid-source MOCVD apparatus. T. Yamaguchi *et al.*

T. Yamaguchi *et al.*[1] The best T_c and J_c values for 2.5 μm YBCO depositions onto 16 cm long YSZ/Hastelloy tapes have been 84 K and 21,000 A/cm^2 (77 K) respectively. A liquid-source MOCVD technique with plasma enhancement (Fig. 2.3) has been investigated by J. Zhang *et al.*[2] The process bears strong resemblance to that described by Matsuno *et al.*, but also introduces an rf plasma of O_2 and N_2O reactant gases into the deposition zone. In addition, isopropanol and tetraglyme are added to the THF/diketonate mixture to lower the solution evaporation rate and increase Barium precursor stability. Half-micron films have been deposited onto $LaAlO_3$ crystal at slow rates of 0.2 to 0.5 μm/hour yielding T_c=89 K and excellent J_c=1,000,000 A/cm^2 (77 K).

1. T. Yamaguchi, Y. Iijima, T. Ohyoshi, O. Kohno, N. Hirano, and S. Nagaya.
2. J. Zhang *et al.* Appl. Phys. Letters, Vol. 61, No. 24, 1992.

2.2 Aerosol-assisted MOCVD

An AACVD system (Fig. 2.4) was constructed by K. Salazar *et al.*[3] to address the problems of

3. K. V. Salazar *et al.* Physica C, 198, 1992.

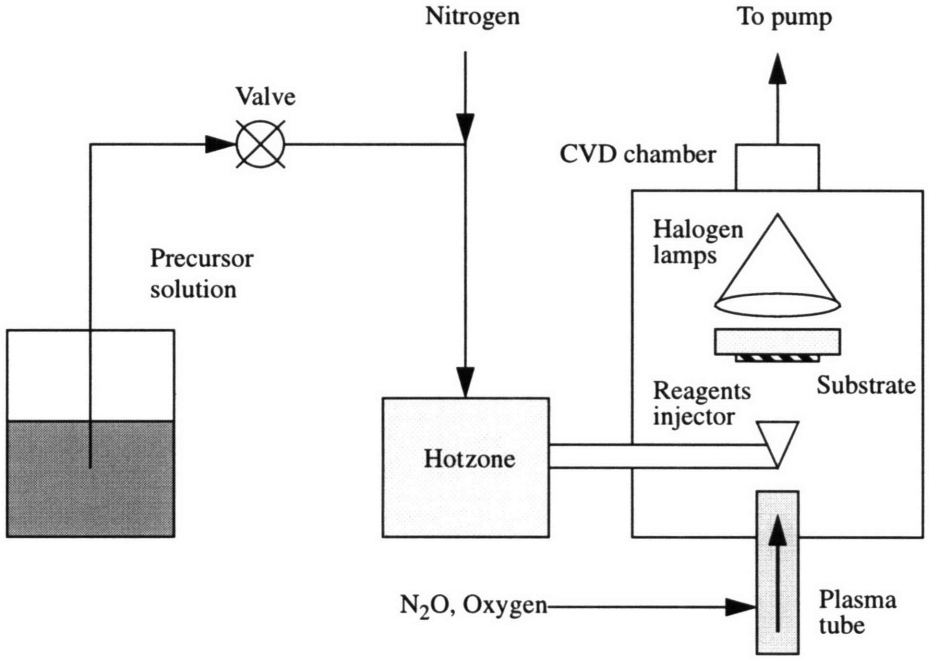

Fig. 2.3. Apparatus for liquid-source MOCVD with plasma enhancement. J. Zhang *et al.*

poor volatility and thermal degradation of precursor species, particularly $Ba(tmhd)_2$. The system eliminates the standard thermal vaporization unit, and instead depends upon a preheating zone within a hot-wall furnace to vaporize the output of an aerosol generator just moments before deposition onto a heated substrate. Because this configuration subjects the precursors to a residence time of less than half a second, in principle thermally sensitive, poorly volatile precursors can be used. Salazar finds that the very reproducible results of the AACVD process are due in no small part to these sub-second residence times at high temperature. $YBa_2Cu_3O_{x-7}$ films with T_c in excess of 88 K and transport critical current densities of 220,000 A/cm^2 (75 K) at self-field have been reported. In addition, the reactor can operate at atmospheric pressures and is therefore inexpensive to build and simple to operate. On the down side, good results with $LaAlO_3$ substrates have only been obtained by subjecting the films to a time-consuming two-step anneal procedure after the initial deposition process.

2.3 Powder-source MOCVD

Exceedingly rapid film deposition rates of 200 to 240 μm/hour have been achieved using a free-flowing powder-source MOCVD technique (Fig. 2.5) developed by Lackey *et al.*[1] A finely ground mixture of Y, Ba, and Cu β-diketonate precursors is dispersed into a high-flow

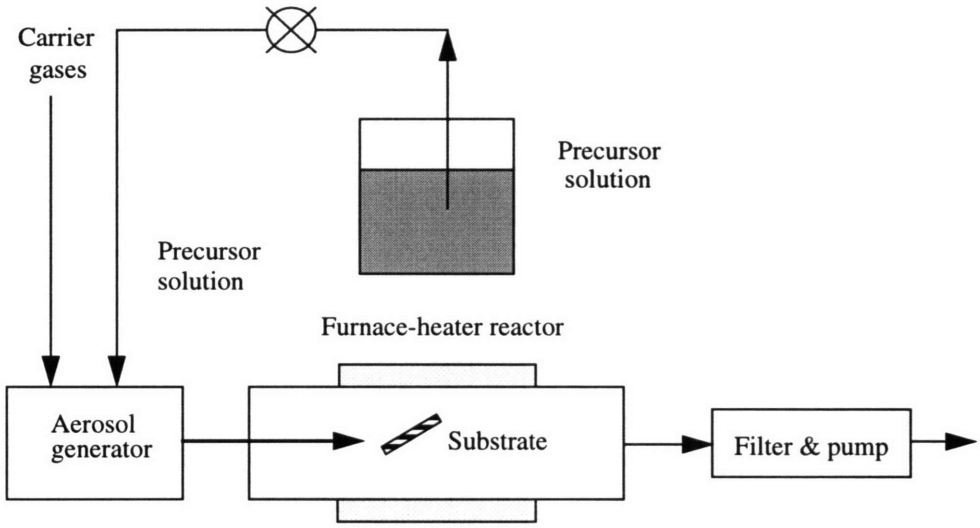

Fig. 2.4. Schematic of aerosol-assisted MOCVD apparatus. K. Salazar *et al.*

(5 L/min) argon carrier gas stream by a modified vibratory feeder and is pneumatically carried directly to a substrate within a hot-wall furnace reactor. Similar to the approach taken by Salazar *et al.*, this system lacks a separate thermal vaporization unit located just upstream from the furnace. Instead, a pre-heating zone at the entrance of the furnace vaporizes the incoming powder particles just moments before deposition onto the heated substrate. The apparatus is capable of evenly coating 5 planar substrates placed perpendicular to the vapor stream and mounted one behind the other without a significant "shadow effect". T_c for $YBa_2Cu_3O_{x-7}$ films produced by this process have been relatively poor at 80-84 K, and critical current densities have not been published.

Powder-source MOCVD offers distinct advantages over conventional liquid delivery techniques including extraordinarily high deposition rates, high product throughput, a reduced number of process control variables (because vaporizers are not used), and near elimination of premature thermal decomposition of reagents (thanks to shortened residence times). Because the powder-source process is less dependent on the volatility of the precursor reagents, it is hoped that cheaper acetylacetonates can eventually be used in place of more volatile and expensive tmhd (tetramethylheptandedionate) complexes. This substitution alone could result in a cost savings of approximately 4000%.

Unfortunately, the technique has major drawbacks as well. As a general rule, free powders are difficult to handle and cannot be dispersed in a dependable and continuous particle by particle manner into a gas stream. Yttrium, barium, and copper β-diketonate materials are sticky and tend to conglomerate into particles of unpredictable size and species content, and then these conglomerated particles tend to segregate during mixing and vibratory processes.

1. W. J. Lackey *et al.* Appl Phys. Letters, Vol. 56, No. 12, 1990.

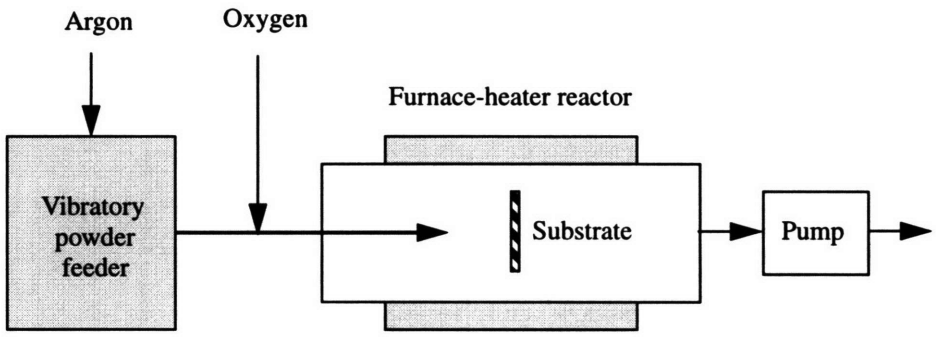

Fig. 2.5. Free-flowing powder-source MOCVD apparatus. W. J. Lackey *et al.*

Very high carrier gas flow rates are required to prevent heavier Cu-laden conglomerative particles from settling out of the gas stream and thereby altering the stoichiometry of the films. Delivery lines and chambers coated with finely divided particles can spontaneously explode when oxygen is introduced into the system at the wrong time, location, and temperature. Stainless steel structures must be grounded to prevent static discharge. And finally, the quality of the superconducting films produced by the powder-source technique cannot be determined because J_c values were never reported by Lackey *et al.*

2.4 Gas-free (bubbler) MOCVD

An MOCVD apparatus (Fig. 2.6) developed by Schulte *et al.* (Appl. Phys. Letters, Vol. 59, No. 7, 1991) does not require carrier gases for the transport of vaporized precursor materials to the heated substrate. Instead, precursor transport is entirely diffusion controlled. Solid plugs of Y, Ba, and Cu β-diketonate precursors are individually vaporized in crucibles heated to their respective sublimation temperatures. The expanding vapors are funneled up a hot-walled chimney and are then deposited onto a substrate. Oxygen flow during cooling to room temperature is provided by a coaxial oxygen

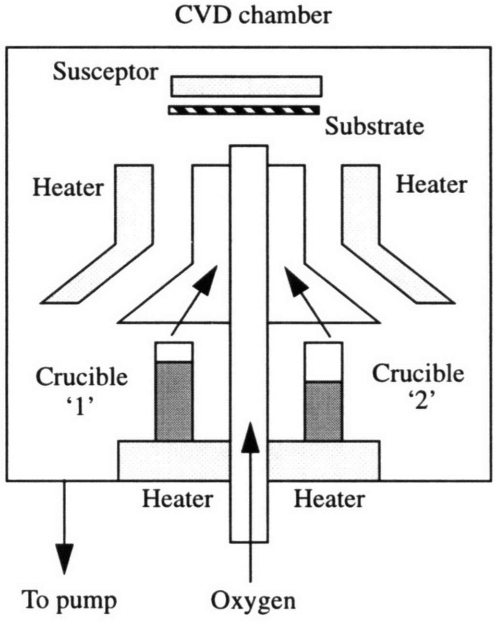

Fig. 2.6. Schematic diagram of carrier gas-free MOCVD apparatus. B. Schulte *et al.*

pipe. The system has produced $YBa_2Cu_3O_{x-7}$ thin films of unspecified thickness on $SrTiO_3$ substrates with very high T_c and J_c values of 91.8 K and 1,300,000 A/cm^2 (77 K) respectively. Schulte surmises that moderately high 2 μm/hour deposition rates are due in large part to the fact that no carrier gases have been used. This results in a higher density of metalorganics in the gas phase.This MOCVD technique boasts the advantages of extreme simplicity, very few operational control variables, and compact size. However, it is unclear whether films of good quality can be obtained once thermal degradation of the precursors in the crucibles occurs. It is likely that thermal effects are significant after the first few minutes of a run.

2.5 Solid-source MOCVD

$YBa_2Cu_3O_{x-7}$ films on $LaAlO_3$ substrates with critical current densities as high as 4,000,000 A/cm^2 (77 K) and transition temperatures up to 91 K have been achieved using a solid source MOCVD technique (Fig. 2.7) developed by

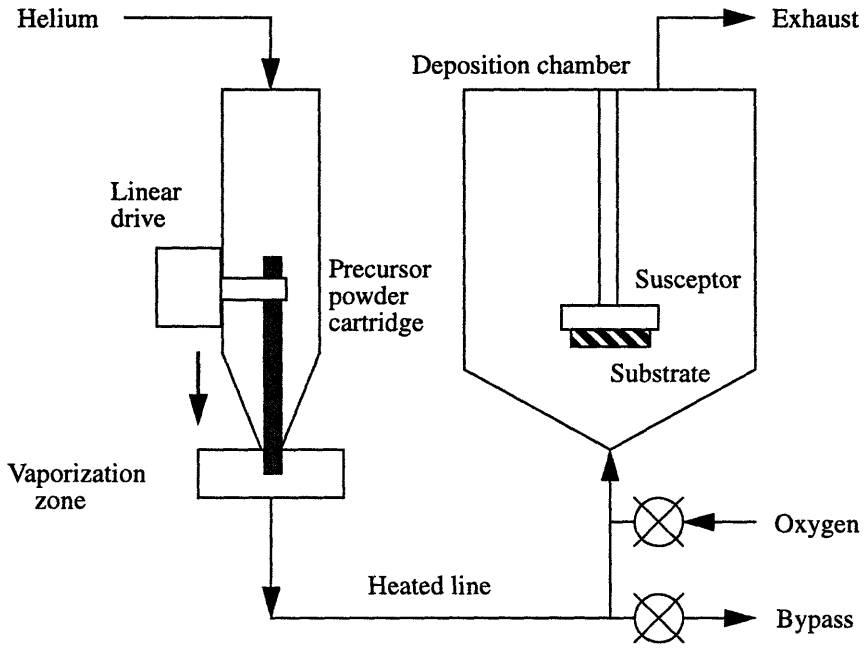

Fig. 2.7. Schematic of solid-source MOCVD apparatus. R. Hiskes *et al.*

Hiskes *et al.*[1] The 0.2 - 0.7 μm films exhibit dc and rf properties comparable to the best films grown by other techniques. A 4 mm precision-bore quartz tube is packed with a mixture of Y, Ba, and Cu β-diketonate precursors and is slowly driven through a sharp temperature gradient created by a 300 °C quartz halogen lamp placed directly below a water-cooled jacket. The lamp progressively vaporizes the precursor pack within the tube at the rate of 0.1 to 5 mm/min,[2] with a more typical tube velocity[3] of 0.5 mm/min. Typical precursor material vaporization rates by volume are calculated to be 0.105 mm^3/second. The vapors are swept through a heated line to the substrate surface by helium carrier gas in approximately one second. Films are grown on 700-710 °C substrates at 4 Torr and are then oxidized *in situ* as the reaction chamber is cooled and brought to 760 Torr under oxygen.

The Hiskes deposition system is simple and compact. Film composition and growth rate can be controlled independently, and neither is influenced by the temperature profile of the heating zone or the volatilities of the organometallics in the precursor mixture[4]. Also, fully oxidized superconducting films can be created *in situ* without a separate anneal procedure. However, deposition rates are rather slow, ranging from 0.3 to 0.8 μm/hour, and continuous-process runs can not be supported.

This reactor design was developed in an attempt to eliminate problems with the instability of the barium precursor, and has been met with much success for the production of large area YBCO films up to 100 mm in diameter. However, it must be noted that precursor residence times at elevated temperatures are not particularly short. Temperature gradients at the tip of the precursor cartridge can be as steep as 100 °C/mm[5] in theory, but are typically about 13 °C/mm.[6] Assuming that the precursor pack is vaporized at a rate of 0.5 mm/min, all precursor materials with in the tube will spend at least 50 seconds at temperatures within just 6 degrees of sublimation temperatures. All the while, thermal degradation of the precursors is proceeding.

The Hiskes system is currently under investigation by several laboratories[7]. Also, the design has been used to produce a variety of technologically important electro-optic materials in addition to YBCO superconducting films.[8]

2.6 Summary

Optimal precursor material delivery is the key to a successful superconductor formation process. Currently, YBCO MOCVD systems offer four kinds of precursor delivery techniques: liquid-source delivery, free-flowing powder delivery, bubbler delivery, and solid-source delivery. Liquid-source systems are undesir-

1. R. Hiskes *et al.* Appl. Phys. Letters, Vol. 59, No. 5, 1991.
2. R. Hiskes *et al.* Mat. Res. Soc. Symp. Proc., Vol. 335, 1994.
3. G. Meng *et al.* Appl. Phys. Letters, Vol. 63, No. 14, 1993.
4. G. Meng *et al.* Appl. Phys. Letters. Vol. 53, No. 14, 1993.
5. R. Hiskes *et al.* Mat. Res. Soc. Symp. Proc., Vol. 335, 1994.
6. Z. Lu *et al.* Appl. Phys. Letters, Vol. 67, No. 5, 1995.
7. G. Meng *et al.* Physica C, Vol. 214, 1993.
8. R. Hiskes *et al.* Mat. Res. Soc. Symp. Proc., Vol. 335, 1994.

able because their success depends on the choice of a suitably volatile solvent that does not contaminate the final product. At present, no such suitable solvent has been found, as evidenced by relatively poor published critical current densities. These systems also tend to be complex, expensive, and difficult to clean and maintain. Free-flowing powder systems are at a disadvantage because sticky YBCO precursor materials tend to conglomerate and do not "free-flow" very well at all. And because particles tend to slough away from the main powder reservoir in an uncontrollable and unpredictable manner, large numbers of particles must be released per unit time to even out the inconsistencies. Considering that YBCO precursor materials may cost $15-20 per gram, such a delivery technique is commercially undesirable. Bubbler delivery is unacceptable simply because the process subjects the precursor materials to excessive thermal degradation, and thermally-regulated diffusion processes are difficult to control. And finally, solid-source precursor 'cartridge' delivery techniques --- like that proposed by R. Hiskes -- offer fine delivery control and excellent product quality, but are inherently flawed because they, too, subject the precursor materials to reduced, but still excessive thermal degradation.

For the most part, scientists who have taken the time to thoroughly analyze these systems know, or least think they know, what the problems are. Some have even gone so far as to mathematically model many of the failure modes. But rigorous analysis of such faulty deposition systems may be premature. For example, Meng *et al.*[1] have developed a sophisticated model of the "melt wedge" of degrading and vaporizing precursor materials that occurs in the Hiskes system due to the close juxtaposition of the feeder and vaporization mechanisms. If it was known, beyond a reasonable doubt, that a solution must be found within the confines of a system design that exhibits such close juxtaposition, such a model would be very helpful. But if the search space has not yet been exhausted --- and almost certainly it has not --- it may be more valuable to find an alternative to the close juxtaposition that is causing the melt wedge in the first place. Chapter 3 is devoted to the search for alternative solutions to these kinds of problems.

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1. G. Meng *et al.* Appl. Phys. Letters, Vol. 63, No. 14, 1993.

3 In search of a better deposition system

As shown in Chapter 2, there is a distinct need for a YBCO deposition process that turns out a superior superconducting product at a significantly reduced cost. However, designing a better deposition process is a complicated matter that requires a thorough understanding of the strengths and weaknesses of past system designs. Many critical, and often conflicting performance and economic considerations must be taken into account. This chapter presents the most significant of these considerations and highlights enhancements that may improve the product performance and economic viability of future YBCO deposition systems.

3.1 Source materials

The efficacy of any CVD process depends on satisfactory vaporization of source materials. CVD processes for the deposition of semiconductors utilize gas or liquid sources with high vapor pressures and stabilities. These sources are readily vaporized without significant thermal degradation. However, CVD for the deposition of YBCO superconductors is made significantly more difficult because source materials are generally unstable and relatively involatile. The severity of this problem cannot be over emphasized. Source stability and volatility is critical to deposition rate control, and therefore stoichiometry control of the deposited film. An optimal YBCO deposition process would do as much as possible to both manage and enhance source stability and volatility. A logical first step toward process enhancement would involve the choice of a suitable precursor material. Hårsta and Carlsson[1] have found that YBCO precursors with low carbon-hydrogen ratios exhibit small regions of thermal stability and readily degrade near vaporization temperatures. Fluorine-containing precursors, which were popular until very recently, have low C/H ratios and small regions of stability, and should be avoided. Also, these fluorine-based precur-

1. A. Hårsta *et al.* Journal of Crystal Growth, Vol. 110, 1991.

sor materials require at least one extra time-consuming annealing process in O_2 for proper superconductor crystal formation. Non-fluorine β-diketonate chelates bearing *t*etra*m*ethyl-*h*eptane-*d*ionato radicals (also known as *dipivoloylmethane* or dpm) --- like $Y(tmhd)_3$, $Ba(tmhd)_2$, and $Cu(tmhd)_2$ --- exhibit significantly larger regions of thermal stability and have become the precursor materials of choice. Unfortunately, this increased stability comes with a significantly increased price tag that averages around $15 per gram. And these tmhd sources do have their problems. For example, $Ba(tmhd)_2$ has been found to have an irreproducible and variable transport rate because of gas phase and solid state oligomerization and hydrolysis reactions.[1] However, it has been suggested that even better source materials can be found. $Ba(tmhd)_2$ could possibly be replaced by substantially more stable sources like $Ba(tmhd)_2(phen)_2$[2] or barium amine-sequestered tmhd (bis (2, 2, 6, 6,-tetramethl - 3,5 - heptanedionato)).[3] Amine-sequestered materials are still in the developmental stages and currently cost about $40 per gram. Deposition temperatures can possibly be lowered by about 10 degrees by replacing $Cu(tmhd)_2$ with copper acetylacetonate,[4] which has the effect of raising the carbon-hydrogen ratio and greatly reducing the cost of the copper source. And finally, halide-based precursors have been shown to exhibit large regions of deposition stability when total pressures are *increased*. With further research, halide-containing precursors may prove to be an enticing alternative to β-diketonates. However, until these alternative sources become widely studied and understood, tmhd complexes of Y, Ba, and Cu are the most reliable that the field has to offer.

But in what form should these tmhd sources be introduced into the MOCVD system? Liquid or solid? As mentioned previously, liquid-source systems are generally undesirable. It appears that precursor solvents tend to poison superconducting films, which can have a disappointing effect on critical current densities. As far as the author is aware, 310 kA/cm^2 (77 K) is the highest current density that has been supported by a YBCO superconductor produced by a non-assisted liquid-source deposition system. With plasma-assistance, J_c values for a liquid-source system can be pushed to about 1 million A/cm^2. But even a simple solid-source bubbler system can often produce a superconducting tape with J_c values in excess of 1.2 million A/cm^2, and the Hiskes solid-source cartridge delivery system boasts a J_c of 4 million A/cm^2. Until a suitable, non-contaminating solvent can be found, it is reasonable to suggest that an optimal deposition system would use a solid-source delivery mechanism that keeps tmhd precursor materials in the solid phase until the very moment of vaporization.

The volatility of precursor materials, like those in the tmhd family, can be enhanced by increasing the surface area directly exposed to vaporizing radiation, low system pressures, and the evaporative effects of carrier gases. Previous MOCVD system designs have achieved a significant increase in surface area by several methods. Some liquid delivery systems use an upstream atomizer to generate small droplets that are subsequently vaporized in a vaporization unit. A few aerosol-assisted liquid delivery

1. K. V. Salazar *et al.* Physica C, 198, 1992.
2. T. Yamaguchi, Y. Iijima, T. Ohyoshi, O. Kohno, N. Hirano, and S. Nagaya.
3. S. A. DiCarolis.
4. A. Hårsta *et al.* Journal of Crystal Growth. Vol. 110, 1991.

systems use a supersonic nozzle to spray millions of 10-20 μm droplets of precursor solution directly into the deposition chamber.[1] The Lackey free-flowing powder delivery system features a vibratory feeder device that was designed to disperse fine particles into a carrier gas stream. It is worth noting that all of these delivery methods are capable of supporting moderate to high deposition rates. On the other hand, Hiskes solid-source and bubbler delivery systems take the opposite approach and tend to confine the precursor materials in cartridges and crucibles until the very moment of vaporization. These delivery systems reduce the total surface area of the precursors exposed to vaporizing effects, and are generally capable of supporting only sub-micron-per-hour deposition rates. In summary, increased precursor surface area correlates to increased volatility of precursor materials, and therefore greater deposition rates. The economic implications of this last statement are significant, especially in light of the fact that slow deposition rates are *the* primary stumbling block to commercial fabrication of mass quantities of high-T_c superconducting tapes, wires, and wafers.

3.2 Control of source material release

High deposition rates are an economically desirable attribute for any deposition system, but control over the quality of the superconducting film cannot be sacrificed to achieve this effect. The degree of control over film quality is directly related to the degree of control over the stoichiometry of the gas phase downstream from the vaporization process, which in turn is dependent upon the degree of control over the release of precursor material from a feeding device. Liquid feeder devices can be very accurate and are capable of releasing very minute streams of liquid into a gas stream. However, a strong case has already been made against the use of solvents in YBCO deposition systems, so there is little choice but to proceed with solid-source delivery techniques.

In general, solid material feeder devices do not enjoy fine resolution control over mass release rate and dispersion. Three methods of solid material dispersion have been presented previously: free-flowing powder, bubbler, and solid-source cartridge feeding devices. Of these three, the vibrating powder feeder used in the Lackey MOCVD system offers the least control over material release rate and composition. In this system, mass flow of source material into a gas stream is regulated by two control variables --- the velocity of carrier gases blowing through the powder reservoir and the frequency of the feeder's vibrating mechanism. Due to particulate conglomerative and segregative effects within the powder reservoir, these two variables do not offer enough control over the release of material from the feeder. As mentioned earlier, the research team attempted to compensate for control errors by releasing large numbers of powder particles into the gas stream per unit time to give some degree of uniformity to the material flow rate. Compositional control is maintained by a single input variable --- the composition of powders premixed together within the reservoir. Vibration-induced segregation of the powdered precursors by particle size, and therefore by species

1. W. J. DeSisto *et al.* Thin Solid Films, Vol. 206, 1991.

content, causes the average composition of the released material to change over time.

Mass flow rate *and* stoichiometry of the gas phase within the bubbler system proposed by Schulte *et al.* is controlled by the temperature of each of three crucibles --- one for each YBCO precursor component. The design is delightfully simple in concept, but maintaining control over a diffusion-regulated process by means of temperature variation is extremely difficult to implement, especially when the volatility of the tmhd precursor materials is constantly changing due to thermally-induced decomposition.

The feeder mechanism developed by Hiskes *et al.*[1] is a relative success because mass flow rate and composition are independent control variables. Mass flow rate is regulated by the velocity of the precursor powder cartridge through a vaporization zone of constant temperature. Velocity control of the powder cartridge is a mechanical problem that is easily solved by any sufficiently accurate linear mechanism. Composition is controlled by the pre-mixture of species packed into the precursor cartridge. Thermally-induced degradation does have an effect on the diffusion rate of precursor materials into the carrier gas stream, but the configuration of the feeder device prevents this effect from *changing* the diffusion rate over *time*. In other words, steady-state vaporization of precursors within the cartridge can be achieved. However, the fact remains that the Hiskes feeder device does thermally degrade precursor materials, and the lost volatility comes with a sizeable cost --- an unacceptably low deposition rate. The bubbler and Hiskes feeder devices exhibit the same flaw. Both systems depend on the vaporization of precursor materials to initiate mass flow to downstream processes. The vaporization mechanisms for complex materials like β-diketonates are not well understood, and are inherently difficult to regulate with a high degree of precision. The Lackey powder feeder device depends on mass flow and release mechanisms that are arguably even more complicated. In fact, an entire branch of science --- particulate science --- has been devoted to the analysis of the kinds of gas-particle and particle-particle interactions encountered within the vibratory feeder.

An ideal YBCO precursor feeder device would only use processes that are well understood and simply controlled to initiate mass flow and release. Mechanical processes --- such as those encountered in machines with gears, flywheels, ratchets, blades, and the like --- are very well understood and are easily controlled by mechanical and electromechanical input signals. At this point, the author would like to propose that all processes implemented in an improved feeder device be inherently mechanical in nature. This mechanical device should be capable of dispensing tiny amounts of material at a constant rate over long periods of time. Something on the order of 0.2 to 3 grams of precursor material per hour is desirable. It would also be beneficial to have real-time control over composition, instead of depending upon a pre-mixture of species to determine a fixed composition. This feature will make it possible to install a feedback loop for precise control of gas phase stoichiometry with minimal time-delay. And finally, in an effort to reduce the complexity --- and therefore the overall operating cost --- of the deposition system, this improved feeder mechanism should

1. R. Hiskes *et al.* Appl. Phys. Letters, Vol. 59, No. 5, 1991.

be capable of independently controlling mass flow *and* composition with only *one* set of input signals.

3.3 Thermal considerations

Tmhd metalorganic complexes may be more stable than fluoride-based precursors, but they are still prone to significant problems associated with degradation and thermally induced decomposition. When held at temperatures high enough for appreciable vaporization, their volatility dramatically decreases over time. Therefore, precursor materials should be subjected to no more than sub-second residence times at or near vaporization temperatures. Of the MOCVD systems discussed so far, only the liquid delivery (with and without aerosol assistance) and powder delivery techniques meet this requirement. Bubbler and Hiskes-style solid-source systems inherently subject precursor materials to long residence times. Short residence times can only be achieved if the source material feeding process is *thermally isolated* from the vaporization and deposition processes. Also, the time interval between the vaporization and deposition processes needs to be very short.

There are additional thermal issues that should also be given consideration. For example, long heated lines between the point of vaporization and the point of deposition upon the substrate are not recommended. Undesirable thermal gradients are more likely to appear within long lines. Thermal gradients should also be avoided at the substrate. The radiation pattern of the susceptor needs to be profoundly uniform (± 5 °C at $T_{sus} \approx 965$ °C) over the entire deposition zone because uneven radiation patterns are likely to result in the production of films with high surface resistance. The susceptor should also be capable of supporting temperature changes while maintaining a uniform radiation pattern. This feature would allow the susceptor to compensate for absorptance changes of the substrate as it becomes coated with YBCO without affecting the surface resistance uniformity of the deposited films.

3.4 Carrier and processing gases

The tmhd family, $Ba(tmhd)_2$ in particular, is unstable under CO_2 and H_2O atmospheres (i.e. air) and should be handled and processed at all times under inert gases. This can be achieved by placing precursor handling and pre-deposition processes (powder mixing, cartridge packing, etc.), precursor bottle storage, and most -- if not all -- of the MOCVD system inside a glove box or similar atmospheric isolation device.

Gas phase composition, pressure, and fluid dynamics can play a significant role in CVD process enhancement. For example, the thermal stability of tmhd precursors can be improved by using N_2O gas instead of O_2 as the oxygen source, and it is suspected that N_2O can even lower deposition temperatures from greater than 720 °C to less than 650 °C.[1] Normally, partial pressures of oxygen in the gas phase should be kept above 50%. However, if N_2O is used, partial pressures can be reduced to less than 40% because only the active oxygen species, instead of all the oxygen molecules, determines the formation of the superconducting phase.[2] Another investigation conducted at

1. A. Hårsta *et al.* Journal of Crystal Growth, Vol. 110, 1991.
2. G. Meng *et al.* Physica C. Vol. 214, 1993.

Harvard[1] found that the volatility of barium metalorganics is enhanced by the addition of amine vapors of NH_3 and NMe_3. The addition of nitrogen Lewis bases to the CVD carrier gas allows barium β-diketonates to be transported in the vapor phase at temperatures as low as 70 °C (1 atm) with no significant decomposition. Also, there is growing evidence that suggests that low (<20 Torr) total pressures during vaporization and deposition have the effect of raising the critical transition temperature for the $YBa_2Cu_3O_{7-x}$ phase.[2]

Because turbulence causes undesirable gas phase reactions, precursor vapors should always be transported in a state of laminar flow (Re < 1000). As precursor vapors leave the heated delivery lines and enter the deposition zone, laminar flow can be maintained by gradually increasing the inside diameter of the deposition chamber at a 15 degree cone angle.[3] Once the vapor stream reaches the substrate, deposition rate is limited by mass transport of the reactive species via diffusion across boundary layers to the substrate surface --- and is independent of substrate temperatures above 600 °C.[4] As schematically shown in Fig. 3.1, it

1. J. M. Buriak *et al.* Mat. Res. Soc. Symp. Proc., Vol. 204, 1991.
2. A. Hårsta *et al.* Journal of Crystal Growth, Vol. 110, 1991.
3. R. Hiskes *et al.* Mat. Res. Soc. Symp. Proc., Vol. 335, 1994.
4. G. Meng *et al.* Physica C, Vol. 214, 1993.

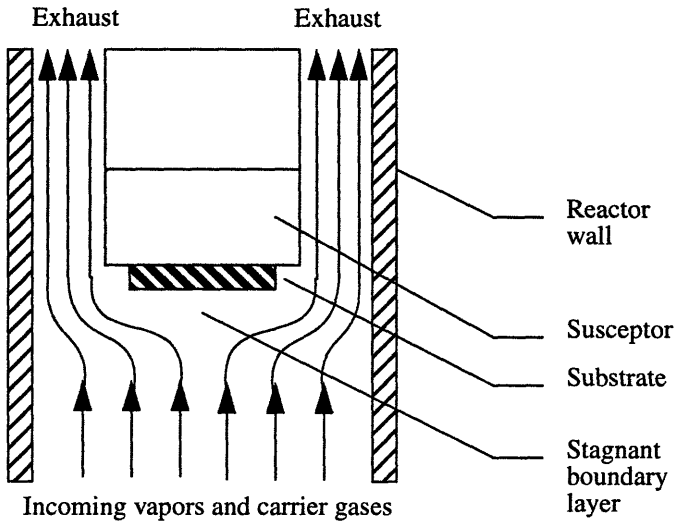

Fig. 3.1. Gas flow pattern in the reactor near the substrate showing the existence of a stagnant boundary layer near the central portion of the substrate. G. Meng *et al.*

has become common practice to align substrates perpendicular the flow of incoming gases. The central part of the substrate is exposed to a stagnant boundary layer of low velocity gas. Because there is insufficient mass transfer of reactive species across the stagnant boundary layer, thinner films are deposited near the center of the substrate. On the other hand, the edges of the substrate are exposed to thinner boundary layers of high velocity gas, and more efficient mass transfer across these thinner boundary layers results in the deposition of thicker films. This indicates that fluid dynamics is still very relevant at low CVD pressures and should be taken into account to obtain uniform film thickness and optimal deposition rates. An improved YBCO deposition system would include geometric features that tend to thin down boundary layers and improve the uniformity of vapor pressures across the entire deposition zone. Such improvements might include the addition of diffusion barriers or baffeling just upstream from the substrate, enlarging reactor diameter, aligning the substrate parallel to the flow of incoming vapors and gases, and altering the cross-sectional profile of the substrate.

3.5 Economic considerations

There are a number of economic factors that should be considered when designing a commercially-viable YBCO deposition system. A deposition system will become a likely candidate for mass market commercial scaleup if, and only if, it is capable of producing a consistently high-quality superconducting product at a significantly reduced cost. The old adage is that 'time is money', and high deposition rates (6 to 50+ μm/hour) will be instrumental to bringing down manufacturing costs. Raw materials like precursor powders and processing gases are expensive and should not be wasted to compensate for system deficiencies. It is hoped that cheaper, more easily handled, and more volatile precursor materials will be discovered in the future. In the mean time, deposition systems need to make the very best use of the precursors that are currently available. Many 'big-ticket' products like magnets and transmission lines will require miles and miles of superconducting wires and tapes. Manufacturing these long lengths will only be possible if the deposition system is capable of supporting continuous process runs that are hundreds to thousands of hours in duration. Other desirable attributes for a potentially commercially-viable deposition system include: low cost deposition equipment; few process control parameters; robust; simple to operate and clean; minimal 'downtime' between deposition runs; can coat multiple irregularly-shaped objects; and modular construction for the simultaneous processing of any number of precursor species.

3.6 Summary

All previously designed YBCO deposition systems leave something to be desired because they all exhibit deficiencies of one kind or another. Typically, deficiencies in these systems fall into one of two broad categories: those deficiencies that cause the system to create a product with poor superconducting performance; and those deficiencies that make the system an unlikely candidate for commercial scaleup. However, some systems exhibit more desirable characteristics and greater promise than others, and it can be argued that the number and magnitude of these positive characteristics are directly correlated to how closely the system design approximates the characteris-

tics of an *"ideal"* YBCO deposition system. In theory, this hypothetical, yet ideal system would retain only the most beneficial attributes of the depositions systems described earlier. In addition, this ideal system would add as many process enhancements and improvements as possible within the confines of the technologically feasible. In this chapter, the author has highlighted the positive aspects of previous deposition system designs and has made recommendations as to how these systems may be enhanced. In essence, these highlights and recommendations, when taken together, help to define the attributes of an ideal YBCO superconductor deposition system. These attributes are summarized in section in 3.7.

3.7 The 'ideal' deposition system

Source materials

- the deposition system should use Y, Ba, and Cu precursor materials that are non-fluorinated β-diketonate chelates bearing *t*etra*m*ethyl-*h*eptane-*d*ionato (tmhd) radicals
- fluorinated precursor species should be avoided
- source materials should not be dissolved with liquid solvents of any kind
- source materials should be kept in the solid phase until the very moment of vaporization
- total surface area of source materials exposed to vaporizing effects should be maximized to increase volatility and deposition rates

Control of source material release

- the source material feeder device should only use processes that are well understood and simply controlled to initiate material release (i.e. mechanical and electromechanical processes)
- the feeder device should be capable of dispensing tiny amounts of material at a constant rate over long periods of time (0.2 to 3.0 g/hour for 100+ hours)
- composition and rate should be independent control variables
- composition and rate should be nearly instantly modifiable via gas phase analyzer feedback loop to rapidly correct for stoichiometry and density errors, which obviates the use of source material reservoirs
- source material mass flow *and* composition should be controlled via only *one* set of input signals

Thermal considerations

- the deposition system should not thermally degrade source materials (i.e. source materials should be subjected to no more than sub-second residence times at or near vaporization temperatures)
- the source material feeding process should be thermally isolated from the vaporization and deposition processes
- if required, only heated lines of minimal length should be implemented between the points of source material vaporization and deposition
- the substrate-heating susceptor within the deposition chamber should be capable of supporting temperature changes while maintaining a uniform radiation pattern across the substrate
- the susceptor should uniformly heat the substrate with compensation for changes in film absorptance

Carrier and processing gases

- source material bottle storage, preprocess handling, and MOCVD system processes should be isolated from outside air at all times

- N_2O and amine vapors should be added to carrier and processing gases to reduce deposition temperature and increase critical transition temperature
- source material vapors should be transported to the substrate in a constant state of laminar flow
- the deposition chamber should include geometric features and substrate-flow alignments that thin down boundary layers and improve the uniformity of vapor pressures across the substrate surface

Economic considerations

- the deposition system should be capable of turning out a superconducting product of consistently high quality (high critical current density, high transition temperature, low surface resistance, sufficient film thickness, etc.)
- the system should be capable of high film deposition rates (6 to 50+ μm/hour) and high product throughput
- the system should be capable of supporting very long (1000+ hour) continuous process runs
- the system should not waste precursor materials and carrier gases to compensate for control deficiencies in source material release rate and composition
- the system should be robust, easy to use, versatile, of modular construction, and inexpensive to manufacture, operate, and maintain

4 The ConBrio MOCVD system

Up to this point, the author has subjected a number of superconductor deposition systems developed by various laboratories to a critical review and analysis. Deficiencies in the design of these deposition processes, and deficiencies in the design of the mechanisms and tools used to carry out these processes, were highlighted. It was found that most of these deficiencies have resulted in either poor end-product performance or unlikely commercial viability. And finally, the attributes of an 'ideal' YBCO superconductor deposition system were put forth. In this chapter, the author will propose a novel YBCO deposition system that should best satisfy the attributes of the 'ideal' deposition system outlined in last section of Chapter 3. In addition, construction of a fully functional prototype deposition system will be documented, and detailed design drawings will be revealed.

4.1 ConBrio: system overview

In an attempt to satisfy as many of the characteristics of the 'ideal' YBCO superconductor deposition system as possible, the author has designed a completely new MOCVD system (Fig. 4.1). The system is named 'ConBrio', which is an allusion to an Italian operatic term meaning "with energy, power, vigor, and speed". ConBrio is composed of three main parts --- a precursor delivery/feeder device, a vaporizer, and a deposition chamber. In theory, these three parts can be separated by arbitrary distances, giving the scientist or manufacturer added installation flexibility when required. However, the author recommends that the vaporizer and deposition chamber be placed in very close proximity to one another to avoid the thermal instabilities of the vapor phase that can develop over longer distances.

The proposed ConBrio MOCVD system uses precursor powders of Y, Ba, and Cu β-diketonates as sources for metallic ions. Because these sources are unstable in air, the entire apparatus is placed within a large glove box or similar atmospheric isolation device. As a first step, precursor powders are packed into hollow stainless steel shells (0.22" ID x 1.40") using a hand press. Under pressures of approximately 8,000 to 12,000 psi, which can

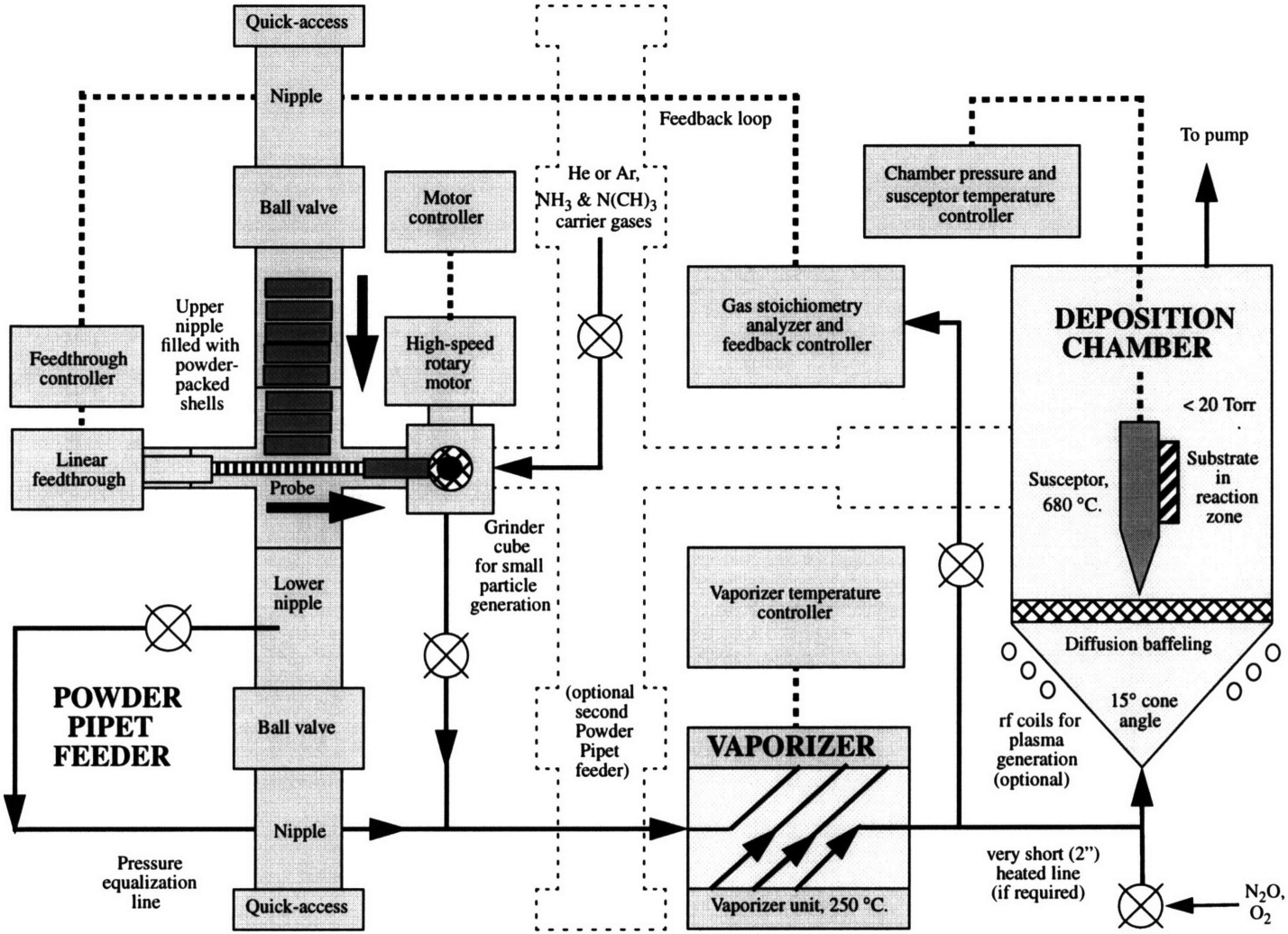

Fig. 4.1. Schematic diagram of the ConBrio MOCVD apparatus. B.N. Hubert *et al.*

be easily generated by nearly any industrial-grade pneumatic hand press, the free-flowing powders are transformed into solid cylindrical packs that are both more hard and less brittle than chalk. The packed shells are loaded into the top of a delivery/feeder device called the 'Powder Pipet'. A supporting ledge within the Powder Pipet precisely positions the bottom-most shell for processing. A rod-like probe, attached to a motorized linear motion feedthrough, is slowly pushed completely through the shell. This action forces the solid precursor pack to slide out from inside the shell and into a high-speed rotary cutting mechanism fitted with blades. The exceedingly slow linear motion of the feedthrough combined with the high speed of the dual rotating blades allows the Powder Pipet to generate sub-micron powder particles. If we assume a probe speed of 21.7 mm/hour, a dual blade speed of 3000 RPM, and an overall material feed rate of 0.105 mm^3/sec -- a material feed rate which is typical for the Hiskes feeder system -- the mechanism should be capable of generating 0.6 μm powder particles. These precursor particulates are swept downstream by a mixture of Ar or He carrier gases supplemented by amine vapors of NH_3 and $N(CH)_3$, and are rapidly sublimed in a 250 °C vaporizer. The precursor vapors then enter an inverted deposition chamber. In an effort to maintain laminar flow, the chamber entrance diameter gradually increases from 14 mm to 200 mm at a 15 degree cone angle. The precursor vapors pass through warm-wall diffusion baffeling just before being deposited onto a 680 °C susceptor-heated substrate aligned parallel to the flow of incoming vapors and carrier gases. Low total pressures (< 20 Torr), which can be regulated by a pressure sensor and controller module, are maintained within the chamber during the entire deposition process by a vacuum pump just downstream from the chamber. The pump also acts an exhaust for excess vapors and carrier gases. When deposition is complete, a superconducting oxide film is formed *in situ* by backfilling the chamber with O_2 and/or N_2O and then cooling to room temperature.

4.2 The Powder Pipet continuous process source material feeder

The Powder Pipet (Fig. 4.2), a table-top device constructed primarily from stock vacuum system components, best resembles the form of a tiny cube-like grinding assembly attached to the intersection of two tubes --- a 'vertical tube' and a 'horizontal tube'.

The vertical tube can assume various lengths, but in its simplest form is approximately 27 inches long. The uppermost extremity of the vertical tube is capped with a size 50 Varian[1] KwikFlange blank, Viton centering ring, quick clamp with wingnut closure, and a KwikFlange to 3-3/8" ConFlat adapter assembly. Continuing from top to bottom, the vertical tube is constructed from a 3-3/8" nipple, 3-3/8" to 1-1/3" reducing cross, another 3-3/8" nipple, size 50 to 3-3/8" ConFlat adapter, Viton centering ring, quick clamp, and a size 50 KwikFlange blank. Although more costly, more convenient access to the top and bottom of the tube can be achieved by replacing the KwikFlange components with MDC[2] 4-1/2" quick-access doors and 4-1/2" to 3-3/8" reducing flanges.

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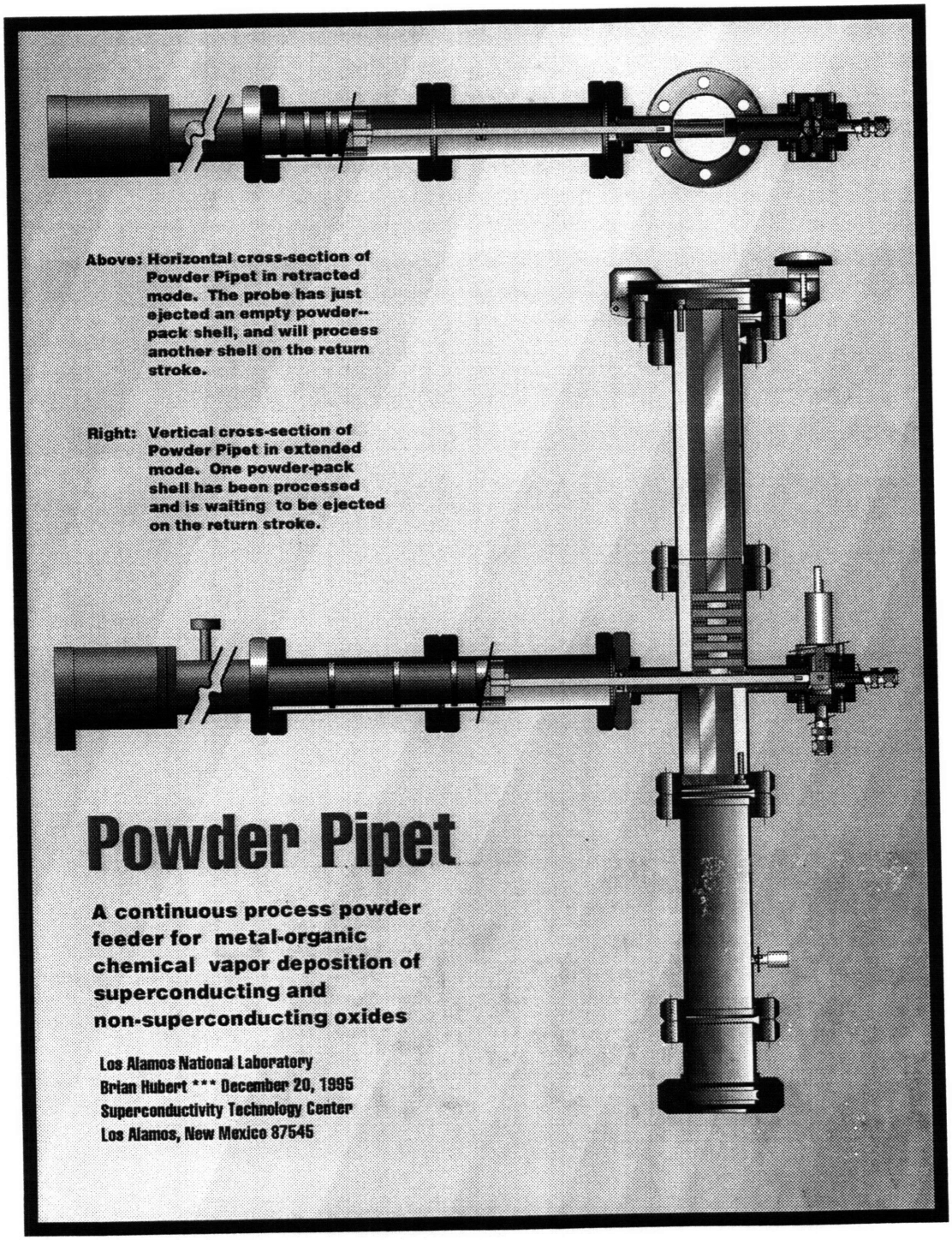
1. Varian Vacuum Products, 121 Hartwell Avenue, Lexington, MA 02173
2. MDC Vacuum Product Corporation, 23842 Cabot Boulevard, Hayward, CA 94545-1651

Figure 4.2.


Above: Horizontal cross-section of Powder Pipet in retracted mode. The probe has just ejected an empty powder--pack shell, and will process another shell on the return stroke.
Right: Vertical cross-section of Powder Pipet in extended mode. One powder-pack shell has been processed and is waiting to be ejected on the return stroke.
Powder Pipet
A continuous process powder feeder for metal-organic chemical vapor deposition of superconducting and non-superconducting oxides
Los Alamos National Laboratory
Brian Hubert *** December 20, 1995
Superconductivity Technology Center
Los Alamos, New Mexico 87545

The purposes of the vertical tube are four-fold: [1] The vertical tube acts as a magazine for the loading and storage of bone-shaped stainless steel shells (Plan 4.A) packed with superconductor precursor powder. [Note: all "Plan" drawings of all custom-machined parts appear at the end of Chapter 4.] The uppermost nipple at the top end of the vertical tube contains a custom Teflon guide (Plan 4.B and 4.C) and fixing anchor plate (Plan 4.D). The shape of the guide closely conforms to the outer dimensions of the shells, preventing the shells from moving laterally out of position; [2] The vertical tube contains a custom Teflon structure that provides a supporting ledge that precisely positions the bottom-most shell for processing. This custom structure, called the reducing cross shell guide (Plan 4.E and 4.F), is installed at the intersection of the two arms of the reducing cross. It's position is fixed by an anchor plate (Plan 4.G) welded to the inner walls of the reducing cross. A vertical section of the vertical tube assembly showing the reducing cross and custom Teflon shell guides is presented in Fig. 4.3, while a horizontal section through the reducing cross is shown in Fig. 4.4; [3] The vertical tube provides a temporary waste receptacle for empty shells that have previously been processed. Processed shells (i.e. shells that are empty) fall into a waste magazine formed by the lower nipple and Kwik-Flange cap assembly; [4] The vertical tube can provide facilities for the removal of empty shells from the apparatus, and loading of new freshly-packed shells into the apparatus, without breaking the vacuum. This fourth attribute is what enables the Powder Pipet to continuously feed precursor materials to the rest of the MOCVD system for tens, if not hundreds of hours without cessation. A clear bore ball valve, a nipple with shell guide, and a quick-access door positioned just above the upper nipple (See Fig. 4.1, not shown in Fig. 4.2) of the vertical tube allows the operator to replenish the supply of packed shells, without losing vacuum. A typical reloading procedure might involve closing the ball valve, increasing nipple pressure to 1 atm, opening the quick-access door at the top of the vertical tube, filling the nipple guide with a load of powder-packed shells, closing the quick-access door, pumping the nipple down to vacuum conditions, and finally opening the ball valve to allow the shells to fall into the reducing cross shell guide. Likewise, a ball valve, a nipple, and a quick-access door positioned just below the lower nipple of the vertical tube allows the operator to follow a similar procedure to periodically remove empty shells that have accumulated in the lower nipple. [Note: the two ball valves, nipples, and quick-access doors are shown in Fig. 4.1, but do not appear in Fig. 4.2. Also, the vacuum pumping devices that must be attached to the ball valves to pump down the nipples are not shown in either figure.]

The horizontal tube of the Powder Pipet is constructed from a pair of 2-3/4" nipples, a 2-3/4" to 1-1/3" reducing flange, and the same reducing cross previously mentioned in the description of the vertical tube. As shown in Fig. 4.2, the left-most end of the horizontal tube is capped with a Huntington[1] 4" motorized linear feedthrough. The speed and direction of the feedthrough is controlled with a precision stepper motor controller. A Teflon-tipped steel probe (Plan 4.H) is attached to the moving end of the feedthrough via probe anchor plate (Plan 4.I). As the feedthrough

1. Huntington Mechanical Laboratories, Inc., 1040 L'Avenida Street, Mountain View, CA 94043

Figure 4.3.

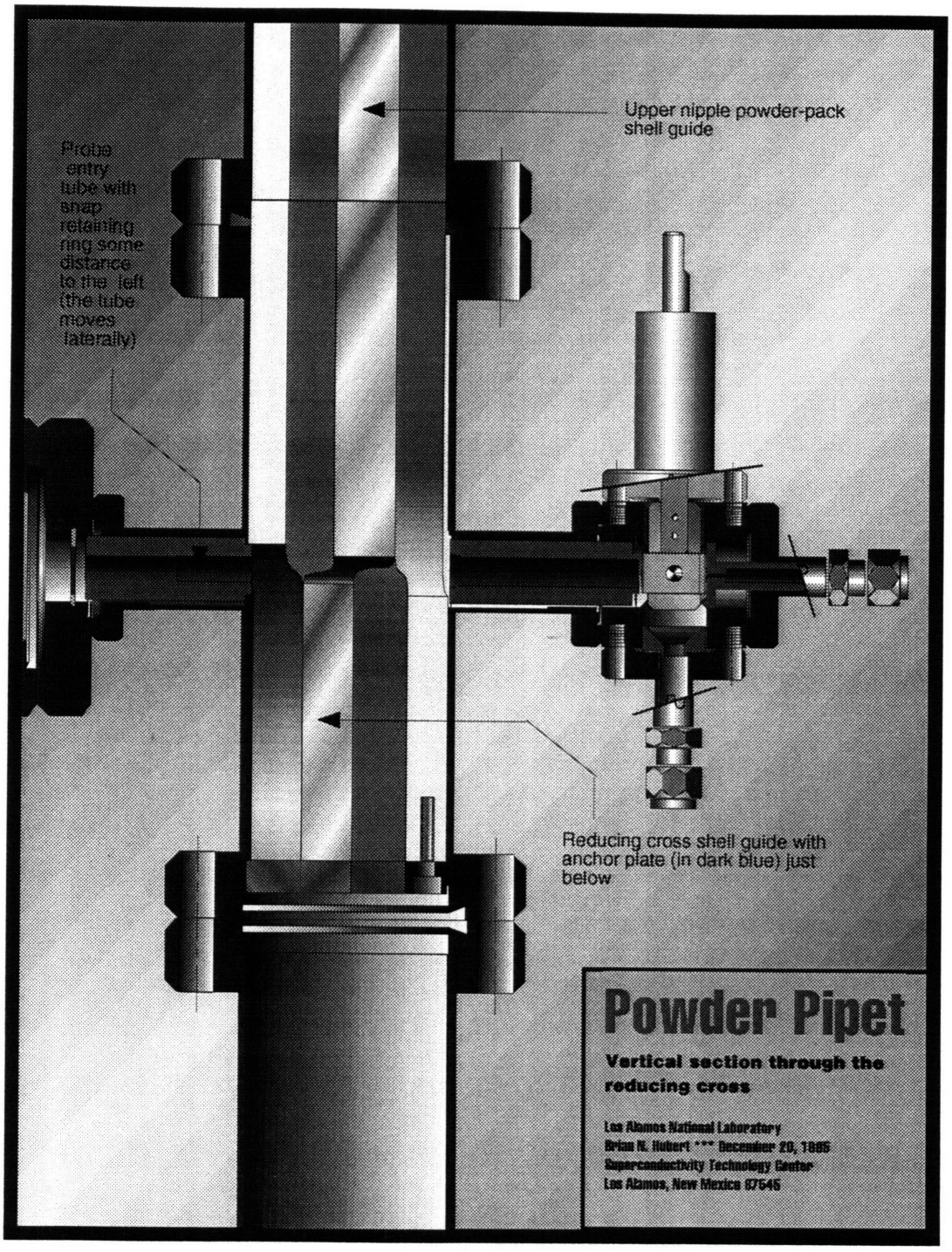
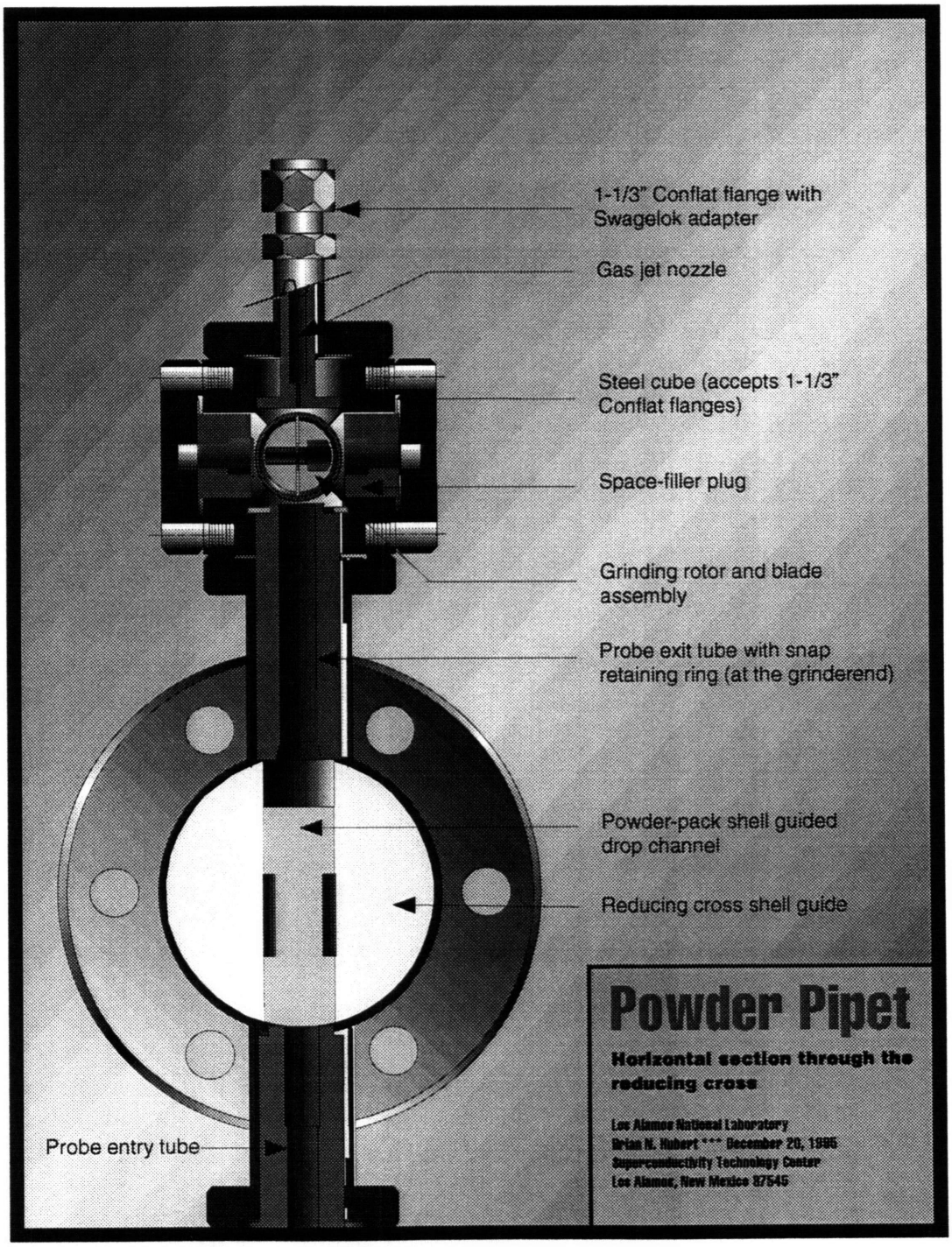

Upper nipple powder-pack shell guide
Probe entry tube with snap retaining ring some distance to the left (the tube moves laterally)
Reducing cross shell guide with anchor plate (in dark blue) just below
Powder Pipet
Vertical section through the reducing cross
Los Alamos National Laboratory
Brian R. Hubert *** December 29, 1995
Superconductivity Technology Center
Los Alamos, New Mexico 87545

Figure 4.4.


1-1/3" Conflat flange with Swagelok adapter
Gas jet nozzle
Steel cube (accepts 1-1/3" Conflat flanges)
Space-filler plug
Grinding rotor and blade assembly
Probe exit tube with snap retaining ring (at the grinderend)
Powder-pack shell guided drop channel
Reducing cross shell guide
Probe entry tube
Powder Pipet
Horizontal section through the reducing cross
Los Alamos National Laboratory
Brian N. Hubert *** December 20, 1995
Superconductivity Technology Center
Los Alamos, New Mexico 87545

extends from left to right inside the hollow nipples, the probe is guided by a probe entry tube (Plan 4.J) and pushes the precursor powder pack out of the bottom-most shell currently positioned on the supporting ledge at the intersection of the reducing cross. The probe is pushed through the shell and continues to move very slowly to the right through the probe exit tube (Plan 4.K) until the entire powder pack has been ground into small-diameter particulates by the grinder assembly (to be described momentarily). Then the linear feedthrough pulls the probe rapidly back to the left. Because the Teflon tip makes an interference fit with the inside diameter of the now empty shell, the shell is pulled to the left along with the probe tip. Eventually, the back end of the shell encounters a stop. Although the shell is now hanging over a shell-shaped hole in the floor of the reducing cross shell guide, it does not fall because the probe tip is still wedged inside. The motorized feedthrough continues to force the malleable probe tip to the left, and so, after traversing the length of the shell, the tip exits the shell. Now completely unsupported, the shell falls through a drop channel to the bottom of the vertical tube. Gravity causes the next packed shell in the que to drop into place onto the supporting ledge just ahead of the probe, and the process is repeated. The probe uses only horizontal motion to process the precursor powder pack, eject the empty shell, and load a new shell into position. The bone shape of the shell allows the probe to complete all these actions by moving back and forth over a distance equal to: [the length of the shell] + [the length of one of the two protruding "cuffs" of the shell (which ideally should be some very *small* fraction of the shell's length)] + [the distance between the front end of the shell when in the maximum forward position and the blades of the grinder (which ideally should be zero)]. In theory, the probe can complete all of the required actions by cyclically traversing a distance that is just slightly greater than one shell length. This short distance is necessary to minimize the retraction time of the probe during the shell ejection and reloading procedure. The movements of the probe and shells over one complete processing cycle are shown sequentially in Figures 4.5 through 4.12.

Construction of the grinder assembly detailed in Figure 4.13 is centered around a tiny steel cube attached to the right arm of the reducing cross. As the probe pushes the precursor pack slowly to the right, the leading edge of the pack is ground into fine, sub-micron powder particles by a pair of steel blades (Plan 4.L) revolving inside the steel cube at approximately 3000 RPM. The blades are secured to the shaft of a Ferrofluidics[1] high-speed rotary motion feedthrough by two halves of a cylindrical blade holder assembly (Plan 4.M, 4.N, and 4.O). The shaft of a Vexta[2] brushless DC motor is attached to the feedthrough via standard flexible shaft coupler and set screws, while the body of the motor is supported by an adjustable L-bracket motor mount (not shown). Rotational speed is controlled via potentiometers built into the body of a Vexta outboard driver box. The powder particles are blown off the cutting blades and are sonically reduced to even smaller particulates by high-velocity carrier gases entering the cube from a 0.02" diameter jet nozzle assembly (Plan 4.P) at rates ranging from 1 to 5 L/min. Particulates are gathered by a funneling assembly (Plan 4.Q)

1. Kurt J. Lesker Company, 1515 Worthington Avenue, Clairton, PA 15025
2. Oriental Motor U.S.A. Corporation, 2580 West 237th Street, Torrance, CA 90505-5217

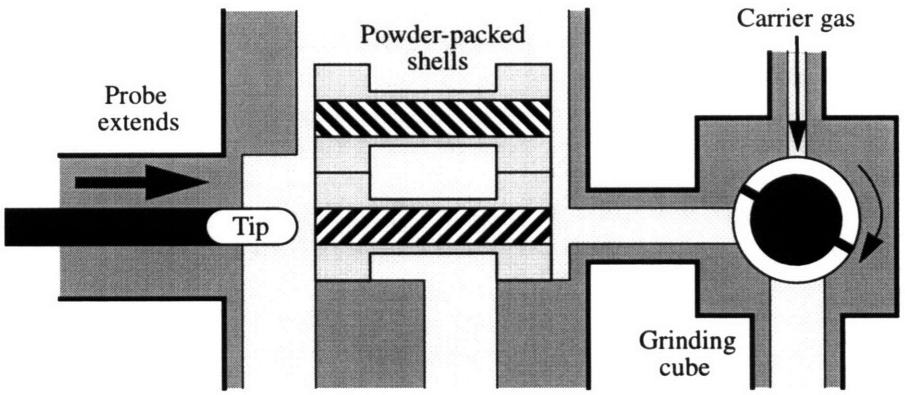


Fig. 4.5. Mechanical action of the Powder Pipet, Step 1: The probe rapidly extends from left to right.

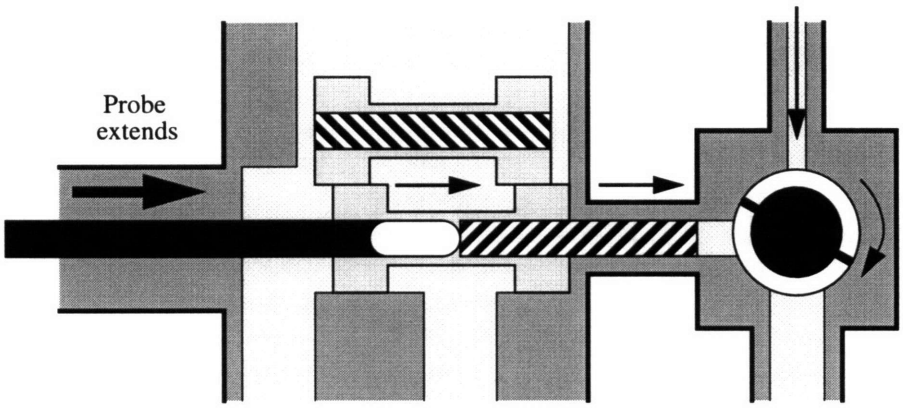


Fig. 4.6. Mechanical action of the Powder Pipet, Step 2: The probe pushes the cylinder of packed powder out of the hollow shell.

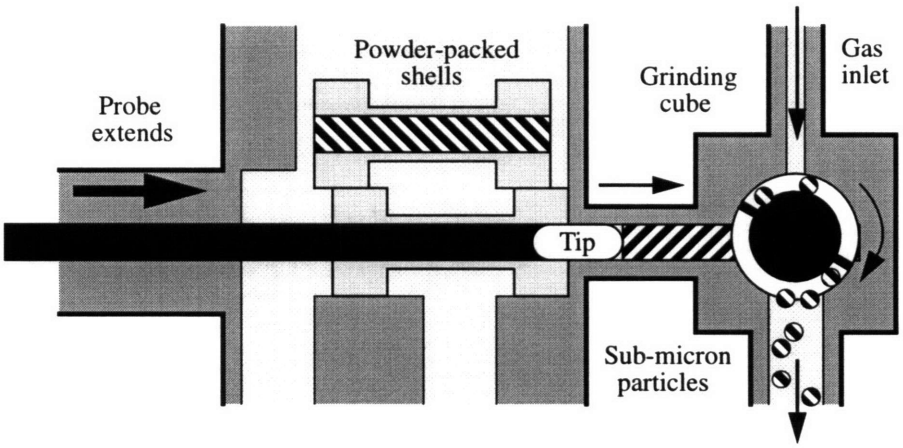


Fig. 4.7. Mechanical action of the Powder Pipet, Step 3: The probe *very* slowly pushes the powder pack into the high-speed grinder. Powder particles are generated.

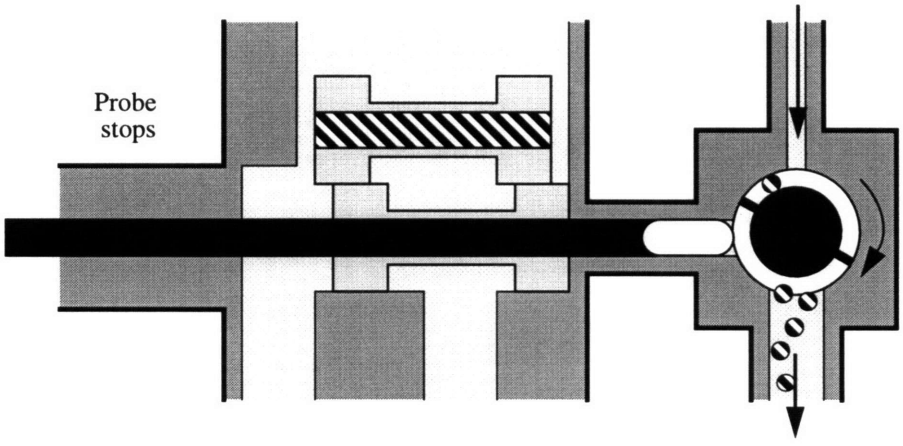


Fig. 4.8. Mechanical action of the Powder Pipet, Step 4: The probe extends to the right until the powder pack has been completely ground into fine particulates.

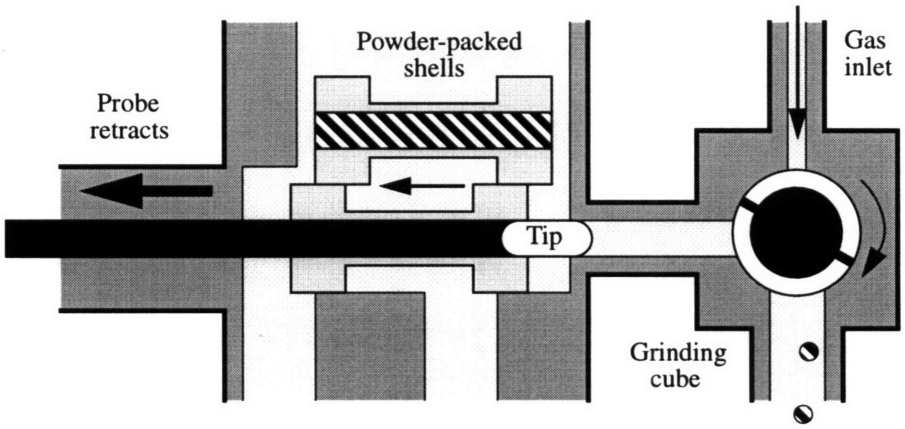


Fig. 4.9. Mechanical action of the Powder Pipet, Step 5:
The probe *quickly* retracts. The interference fit of the probe tip within the shell causes the shell to move as well.

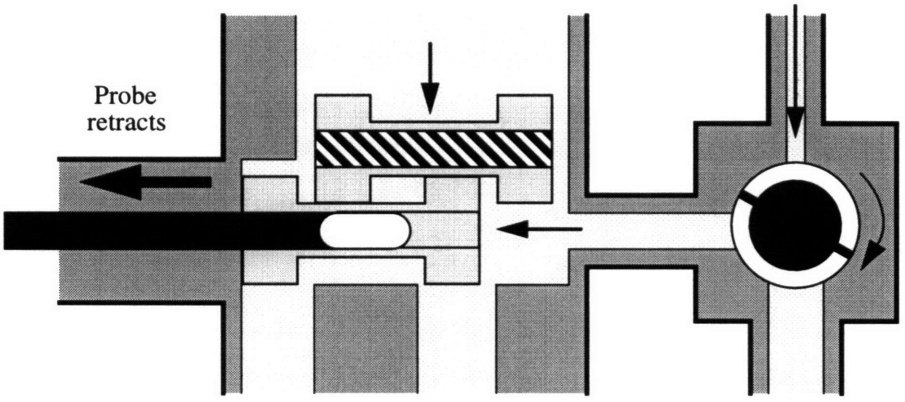


Fig. 4.10. Mechanical action of the Powder Pipet, Step 6:
The back end of the shell hits a stop, but the probe continues to retract to the left. The next shell in the que drops a bit.

Mechanical action of the Powder Pipet (con't)

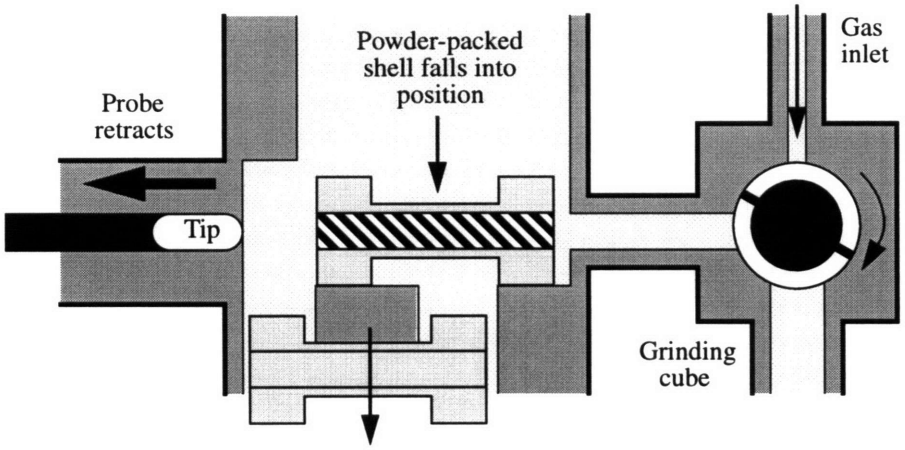


Fig. 4.11. Mechanical action of the Powder Pipet, Step 7:
The probe pulls out of the shell. The empty shell falls through the drop channel. The next packed shell in the que drops into position.

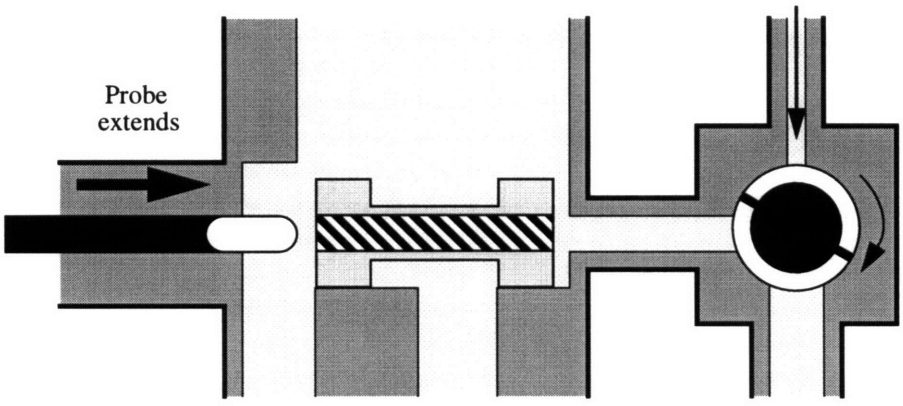
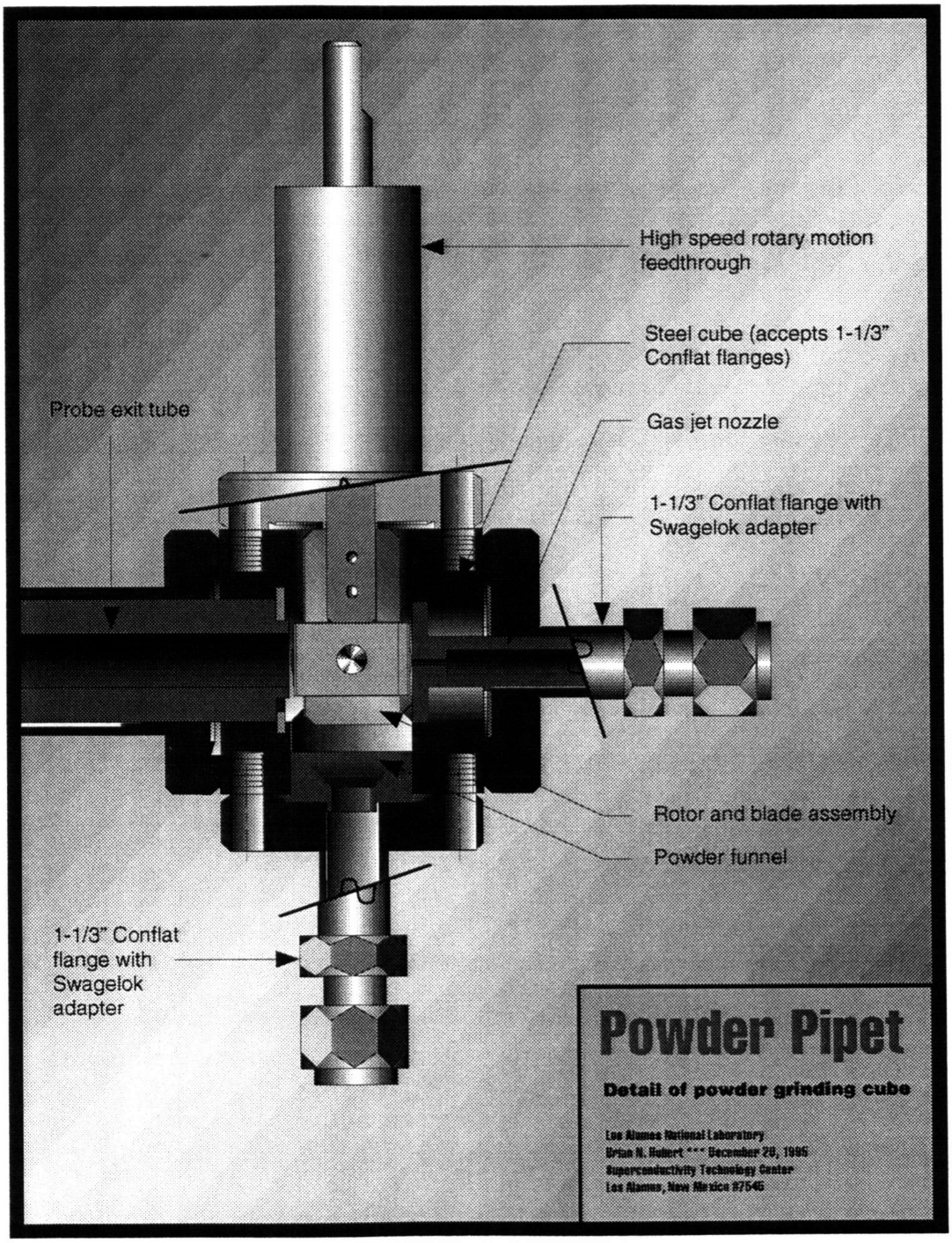


Fig. 4.12. Mechanical action of the Powder Pipet, Step 8:
The probe now extends to the right, and the process begins once more.

Figure 4.13.


High speed rotary motion feedthrough
Steel cube (accepts 1-1/3" Conflat flanges)
Probe exit tube
Gas jet nozzle
1-1/3" Conflat flange with Swagelok adapter
Rotor and blade assembly
Powder funnel
1-1/3" Conflat flange with Swagelok adapter
Powder Pipet
Detail of powder grinding cube
Los Alamos National Laboratory
Brian N. Hubert *** December 20, 1995
Superconductivity Technology Center
Los Alamos, New Mexico 87545

and are immediately whisked downstream by carrier gases. Space filler plugs (Plan. 4.R) are incorporated into the inside faces of the blank flanges attached to the steel cube. These plugs significantly reduce the volume of the cube so that powder particles are more readily directed towards the funnel assembly and then out of the cube. When desired, additional vertical and horizontal tube assemblies can be attached to the cube in place of the blank flanges. When all of the blank flanges are replaced by these assemblies, the single grinder cube can process up to three powder species simultaneously. Mass flow for each of the three species can be regulated independently by adjusting the linear speed of three probes with linear motion feedthrough controllers.

It is important to recognize that the grinder assembly described above is just one of many possible embodiments that can be used to reduce a compressed powder pack to small-diameter particulates. For example, the cutting means can consist of a tiny jet of high-velocity gas impacting upon the leading edge of the advancing powder pack. Alternative methods may incorporate abrading or sonicating devices. The style and method of the cutting means actually employed is of little concern as long as the following criteria are met: (1) the cutting means must be capable of dividing the compressed precursor materials into very small particles at a precisely and reliably controlled rate over a long period of time; (2) the cutting means must sustain a rate of particulate generation that is very low, for example, less than 1 gram per hour; and (3) the cutting means must not thermally degrade or otherwise reduce the volatility of the precursor materials.

4.3 The vaporizer

The particulates generated by the Powder Pipet are transported to a vaporizing unit via carrier gases. The vaporizer may be a simple device constructed from as few as six parts: 1/4" ID coiled tubing, 4" diameter aluminum cylinder and supporting base, coiled heater elements, electrical wall plug, vaporizer temperature controller, and a thermocouple. Powder-laden carrier gases flow through the coiled tubing at a rate of about 1 m/s. Within a fraction of a second, heater elements sublime the powder particles, turning them to vapor. With the addition of nitrogen Lewis bases to the carrier gas stream, sufficient sublimation of the Y, Ba, and Cu β-diketonates should be achieved with vaporizer temperatures no higher than 250 °C.

What has been described above is just one of many possible embodiments for a vaporizer. The style and method of vaporization is of little concern as long as two criteria are met: (1) the vaporizer must be capable of completely subliming small-diameter precursor particulates in less than a second; and (2) after sublimation, precursor vapors should spend no more than an additional half-second residence time in the vaporizer before they enter the deposition chamber. These time durations are approximate, but the general directive is to choose a vaporizing means that inflicts as little thermal degradation upon the precursor materials as possible.

If desired, a feedback control loop can be incorporated into the MOCVD system with the addition of a gas analyzer just downstream

Table 4.1. Major components of the ConBrio MOCVD system

1	Compressed precursor powders packed into shells or cartridges
2	Carrier gas intake line with needle valve
3	Powder Pipet feeder assembly
4	Linear feedthrough stepper motor controller
5	Pressure equalization line with needle valve
6	Vaporizer assembly
7	Vaporizer temperature controller and thermocouple
8	Gas stoichiometry analyzer and feedback controller
9	Inverted deposition chamber with diffusion baffeling
10	Susceptor temperature controller and thermocouple
11	Deposition chamber pressure sensor and controller
12	Exhaust line and filter assembly
13	Vacuum pump
14	Large glove box with inert atmosphere

from the vaporizer. This analyzer would be sensitive to changes in precursor vapor density and stoichiometry, and could then send correction signals to the linear feedthrough controller(s) to speed up or slow down the probe(s), and thereby release more or less powder into the gas stream. An analyzer feedback control loop is presented in the overview schematic of the ConBrio apparatus (Fig. 4.1).

4.4 The deposition chamber

Precursor vapors generated by the vaporizer unit are transported by carrier gases through a very short heated line and then enter the deposition chamber from below. As mentioned previously, laminar flow into the chamber is preserved by a gradual increase in chamber diameter from 14 mm to 200 mm at a 15 degree cone angle. Coils connected to a 13.54 MHz generator may be wrapped around the outwardly tapered section of the chamber entrance to produce an rf plasma for enhancing the desired chemical reactions in the deposition zone. The chamber design also includes geometric features that tend to thin down boundary layers and improve the uniformity of vapor pressures across the entire deposition zone near the substrate. To this end, the chamber incorporates warm-wall diffusion baffeling just upstream from the substrate and alignment of the substrate parallel to the flow of incoming gases. And finally, continuous depositions onto moving, very long substrates are possible if the stationary substrate holder shown in Fig. 4.1 is replaced by an outlay reel and an uptake reel, with moving substrate material held in tension between them as they rotate.

Table 4.2. Powder Pipet custom components

Component designation	Material	Plan No.	Units
VERTICAL TUBE			
Precursor powder-pack shell	st. steel	4.A	10
Upper nipple shell guide	Teflon	4.B, 4.C	1
Nipple guide anchor plate	st. steel	4.D	1
Reducing cross shell guide	Teflon	4.E, 4.F	1
Reducing cross guide anchor plate	st. steel	4.G	1
HORIZONTAL TUBE			
Probe	st. steel & Teflon	4.H	1
Probe anchor plate	st. steel	4.I	1
Probe entry tube	st. steel	4.J	1
Probe exit tube	st. steel	4.K	1
PRECURSOR GRINDER/FEEDER			
Rotor grinding blades	steel razor blade	4.L	2
Blade holder (parts A & B)	st. steel	4.M, 4.N, 4.O	2
Gas jet nozzle	st. steel	4.P	1
Powder funnel	st. steel	4.Q	1
Space filler plug	st. steel	4.R	2
Adjustable L-bracket motor mount	st. steel	not shown	1
Total number of custom parts			**27**

In Chapter 3, it was mentioned that an 'ideal' YBCO MOCVD system should use a substrate-heating susceptor that is capable of supporting temperature changes while maintaining a uniform radiation pattern with compensation for substrate absorptance. At this time, the author can suggest no significant improvements over current state-of-the-art susceptor or heater element designs.

4.5 Construction and testing

A fully functional prototype ConBrio MOCVD system was constructed between October and December of 1995. As shown in Table 4.1, the complete apparatus consists of 14 major components and sub-assemblies. Most of these components were salvaged from laboratory stock piles, and were repaired and/or modified. However, the majority of the author's design efforts were devoted to development of the Powder Pipet feeder device. The Powder Pipet is constructed from a total of 159 parts. This number drops to just 49 parts when minor accessories like nuts, bolts, dowels, and gaskets are left out of the count. Eighteen distinct custom part designs were machined by Mr. Roy Rockage at the Los Alamos National Laboratory, 27 pieces in all (Table 4.2). The remaining 132 pieces were all stock items purchased from various vacuum products vendors like MDC, Varian, Lesker, and Huntington at a total cost of $4045 (Table 4.3). As shown in Table 4.4, the Powder Pipet can be converted

Table 4.3. Powder Pipet stock components

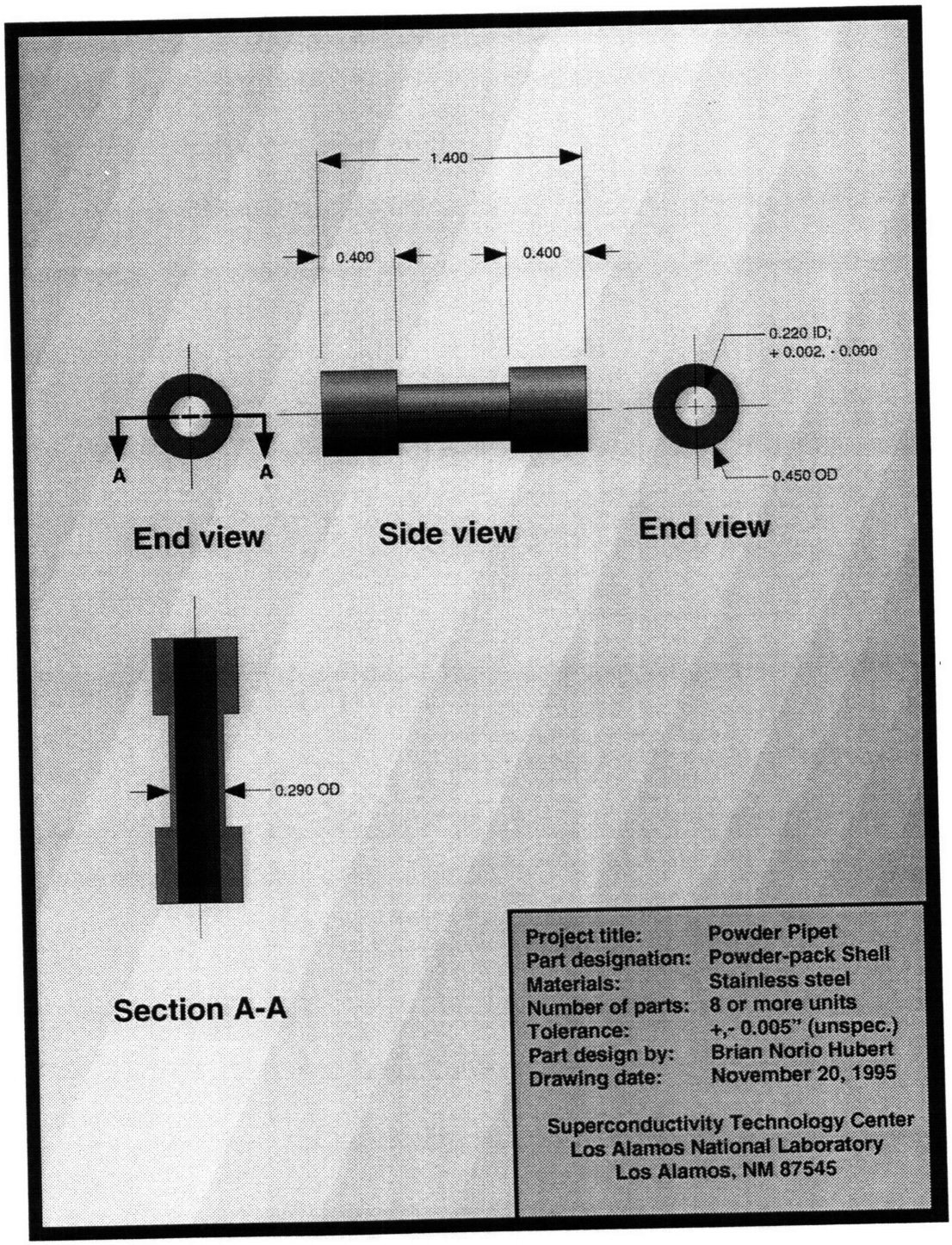
Component description	Units	Vendor	Part No.	Price
VERTICAL TUBE				
KwikFlange size 50 blank	2	Varian	KF50-0000-SB	$ 26
Size 50 Viton centering ring	2	Varian	KC-50-SV	24
Size 50 quick clamp with wingnut closure	2	Varian	KQ-50AWP	30
3-3/8" OFHC copper gasket*	4	MDC	191007	21
KwikFlange to 3-3/8" ConFlat adapter	2	Varian	FA-0338-NW50	220
ConFlat nipple with 3-3/8" flanges	2	MDC	402003	236
5/16-24 x 1-3/4" hex head bolt & nut set*	32	MDC	190006	40
8-32 x 1-1/4" socket head screw*	6	Allied	DY5GY	3
8-32 hex nut*	1	-------	---------	1
Dowels for joining shell guides, 0.90" dia*	3	-------	---------	1
HORIZONTAL TUBE				
4" powered linear feedthrough, 2-3/4" flange	1	Huntington	MFL-275-4	$ 1225
ConFlat nipple with 2-3/4" flanges	2	MDC	402002	110
ConFlat 2-3/4" to 1-1/3" reducing flange	1	MDC	15001	55
2-3/4" OFHC copper gasket*	3	MDC	191004	17
10-32 x 3/4" socket head screw*	4	Allied	DY5HV	2
Snap retaining rings, 0.28" ID min.*	2	-------	---------	1
Probe stop collarand set screw*	1	-------	---------	1
PRECURSOR GRINDER/FEEDER				
6-way steel cube, accepts 1-1/3" flanges	1	MDC	408000	$ 453
1/4" Swagelok to ConFlat 1-1/3" adapter	2	MDC	414000	120
ConFlat 1-1/3" 7065 glass viewport	1	MDC	450000	100
ConFlat 1-1/3" blank	2	MDC	110000	22
1-1/3" OFHC copper gasket*	7	MDC	191000	13
8-32 x 1/2"socket head bolt & nut set*	42	MDC	190000	22
Ferrofluidics rotary feedthrough, 1-1/3"	1	Lesker	FE50-103915	860
Vexta brushless DC motor & driver	1	Oriental	FBL215A-24A	439
8-32 x 3/8" socket head screw*	2	Allied	DY5GR	1
6-32 x 5/16" socket head screw*	1	Allied	DY5FQ	1
2-56 x 3/8" socket head screw*	2	Allied	DY5DR	1
Totals (not including minor accessories*)	**22**			--------
Totals (including all accessories)	**132**			**$ 4045**

Table 4.4. Powder Pipet optional stock components

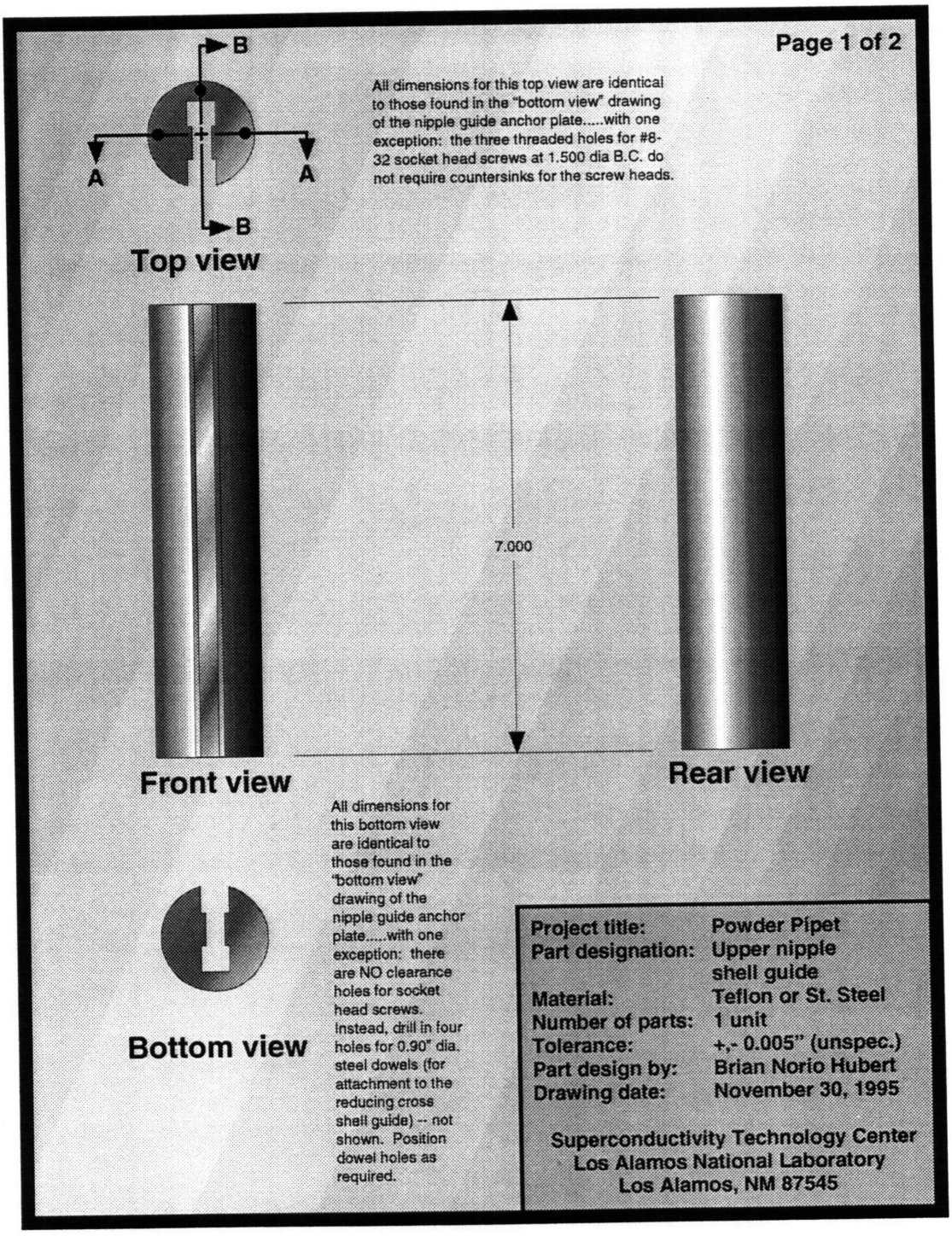
Component description	Units	Vendor	Part No.	Price
FOR CONTINOUS PROCESS RUNS				
ConFlat nipple with 3-3/8" flanges	2	MDC	402003	$ 236
1.875" ID clear bore ball valve	2	Ladish	--------	est. 400
FOR IMPROVED ERGONOMICS				
4-1/2" quick-access door & viewport	1	MDC	665206	$ 650
4-1/2" blank quick-access door	1	MDC	665201	550
4-1/2" to 3-3/8" reducing flange	2	MDC	150009	100
4-1/2" OFHC copper gasket	2	MDC	191009	25
5/16-24 x 1-1/4" hex head bolt & nut set	16	MDC	190003	14
5/16-24 x 2" hex head bolt & nut set	16	MDC	190007	22
Totals for optional additions only	**42**			**$ 1997**

into a true continuous process feeder with improved ergonomics with the purchase of two ball valves, two nipples, and two quick-access doors. This conversion requires the outlay of an additional $1997. The Powder Pipet was assembled and tested under atmospheric conditions. After minimal tweaking, the shell loading, processing, and ejecting actions were found to work nearly flawlessly when the probe was driven by a linear feedthrough controller. The vaporizer and susceptor were also tested in air with good results. Once all lines were connected, the pump was used to bring the pressure of the entire system down to 50 Torr. It is probable that leaks at various points along the lines prevented the system from achieving a better vacuum (<20 Torr). With all components ready to be tested in an actual YBCO deposition run, the LANL Superconductivity Technology Center (STC) director and chief scientist felt it wise to pull the plug on the run. One of the ironies of this powder delivery system is that the performance of the Powder Pipet is quite possibly directly proportional to the likelihood of explosion. The Powder Pipet was designed to disperse exceedingly fine powders into a gas stream. As these particulates get smaller, their combined surface area increases dramatically. An oxygen leak into the wrong portion of the system at the wrong time or temperature could possibly cause powder-coated lines and chambers to spontaneously combust. Concerns of this sort are justified by incidents experienced by Lackey *et al.* among others. It was decided that all test runs should be postponed until the STC can retain the services of an individual with experience in the area of vacuum powder delivery systems, their operation, and appropriate safety precautions. These precautions may include installing the deposition system within a containment cell and grounding steel structures to prevent static discharge.

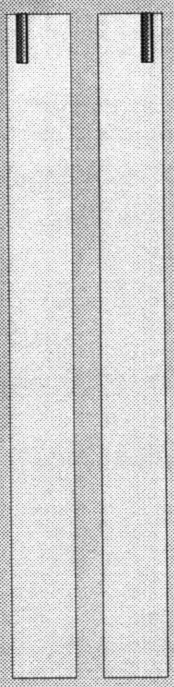
Plan 4.A.


1.400
0.400
0.400
0.220 ID;
+ 0.002, - 0.000
0.450 OD
A
A
End view
Side view
End view
0.290 OD
Section A-A
Project title: Powder Pipet
Part designation: Powder-pack Shell
Materials: Stainless steel
Number of parts: 8 or more units
Tolerance: +,- 0.005" (unspec.)
Part design by: Brian Norio Hubert
Drawing date: November 20, 1995
Superconductivity Technology Center
Los Alamos National Laboratory
Los Alamos, NM 87545

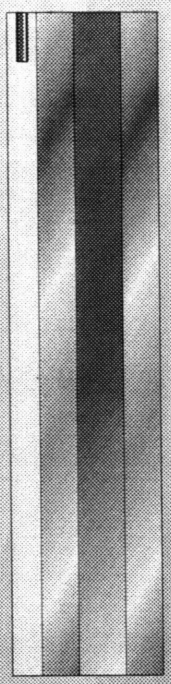
Plan 4.B.


Page 1 of 2
B
A
A
B
Top view
All dimensions for this top view are identical to those found in the "bottom view" drawing of the nipple guide anchor plate.....with one exception: the three threaded holes for #8-32 socket head screws at 1.500 dia B.C. do not require countersinks for the screw heads.
7.000
Front view
Rear view
Bottom view
All dimensions for this bottom view are identical to those found in the "bottom view" drawing of the nipple guide anchor plate.....with one exception: there are NO clearance holes for socket head screws. Instead, drill in four holes for 0.90" dia. steel dowels (for attachment to the reducing cross shell guide) -- not shown. Position dowel holes as required.
Project title: Powder Pipet
Part designation: Upper nipple shell guide
Material: Teflon or St. Steel
Number of parts: 1 unit
Tolerance: +,- 0.005" (unspec.)
Part design by: Brian Norio Hubert
Drawing date: November 30, 1995
Superconductivity Technology Center
Los Alamos National Laboratory
Los Alamos, NM 87545

Plan 4.C.



Section A-A



Section B-B

Note: To simplify the machining procedure, the shell guide can be constructed from two separate pieces. This division should take place along the "cutting plane" for section B-B.

Project title:	**Powder Pipet**
Part designation:	**Upper nipple shell guide**
Material:	**Teflon or St. Steel**
Number of parts:	**1 unit**
Tolerance:	**+,- 0.005" (unspec.)**
Part design by:	**Brian Norio Hubert**
Drawing date:	**November 30, 1995**

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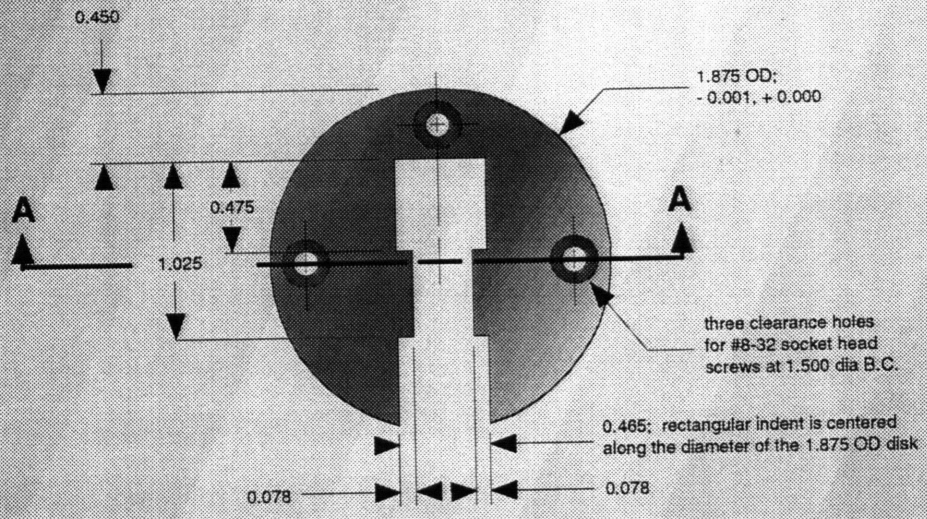
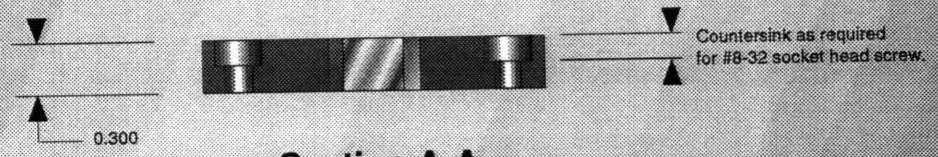
Plan 4.D.



Bottom view



Section A-A

Assembly Notes:

(1) Machine the anchor plate, as indicated in the drawings above.

(2) Screw the anchor plate onto the top end of the nipple shell guide. The anchor plate must be rotated so that the long axis of the rectangular-shaped indent in the disk is parallel to the axis of the nipple shell guide found in the 3-3/8" Conflat flange nipple.

Project title:	**Powder Pipet**
Part designation:	**Nipple guide anchor plate**
Material:	**Stainless steel**
Number of parts:	**1 assembly**
Tolerance:	**+,- 0.005" (unspec.)**
Part design by:	**Brian Norio Hubert**
Drawing date:	**Nov. 28, 1995**

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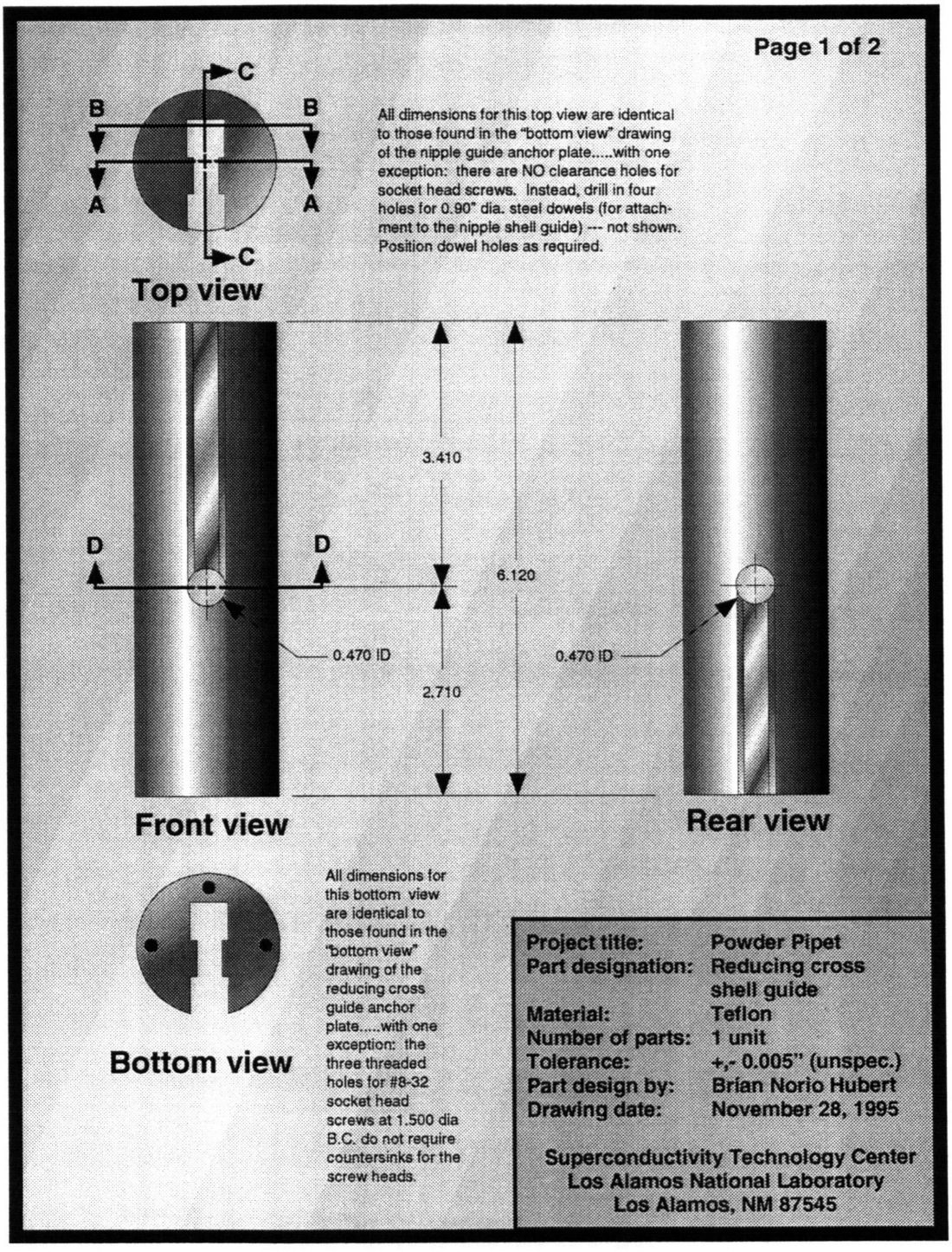
Plan 4.E.


Page 1 of 2
C
B
B
A
A
C
Top view
All dimensions for this top view are identical to those found in the "bottom view" drawing of the nipple guide anchor plate.....with one exception: there are NO clearance holes for socket head screws. Instead, drill in four holes for 0.90" dia. steel dowels (for attachment to the nipple shell guide) --- not shown. Position dowel holes as required.
3.410
D
D
6.120
0.470 ID
0.470 ID
2.710
Front view
Rear view
Bottom view
All dimensions for this bottom view are identical to those found in the "bottom view" drawing of the reducing cross guide anchor plate.....with one exception: the three threaded holes for #8-32 socket head screws at 1.500 dia B.C. do not require countersinks for the screw heads.
Project title: Powder Pipet
Part designation: Reducing cross shell guide
Material: Teflon
Number of parts: 1 unit
Tolerance: +,- 0.005" (unspec.)
Part design by: Brian Norio Hubert
Drawing date: November 28, 1995
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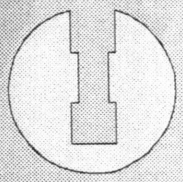
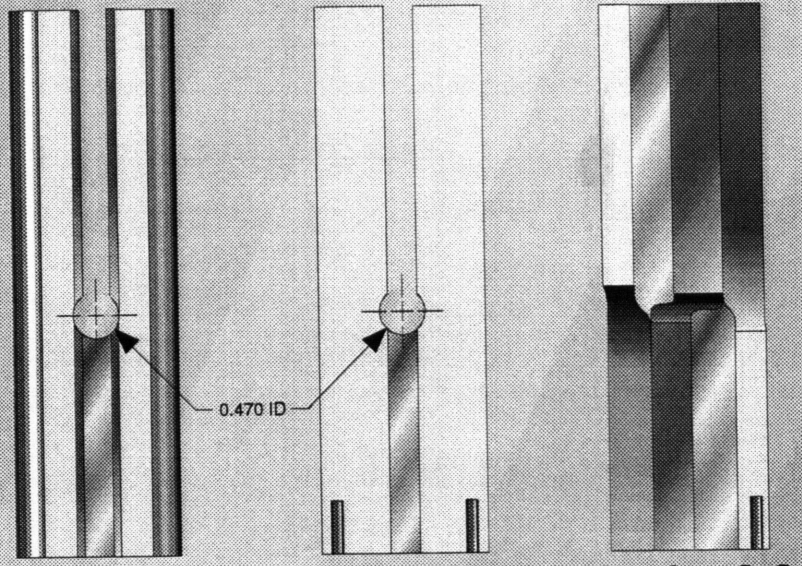
Plan 4.F.



Section D-D



Section B-B Section A-A Section C-C

Note: To simplify the machining procedure, the shell guide can be constructed from two separate pieces. This division should take place along the "cutting plane" for section C-C.

Project title:	**Powder Pipet**
Part designation:	**Reducing cross shell guide**
Material:	**Teflon or St. Steel**
Number of parts:	**1 unit**
Tolerance:	**+,- 0.005" (unspec.)**
Part design by:	**Brian Norio Hubert**
Drawing date:	**November 30, 1995**

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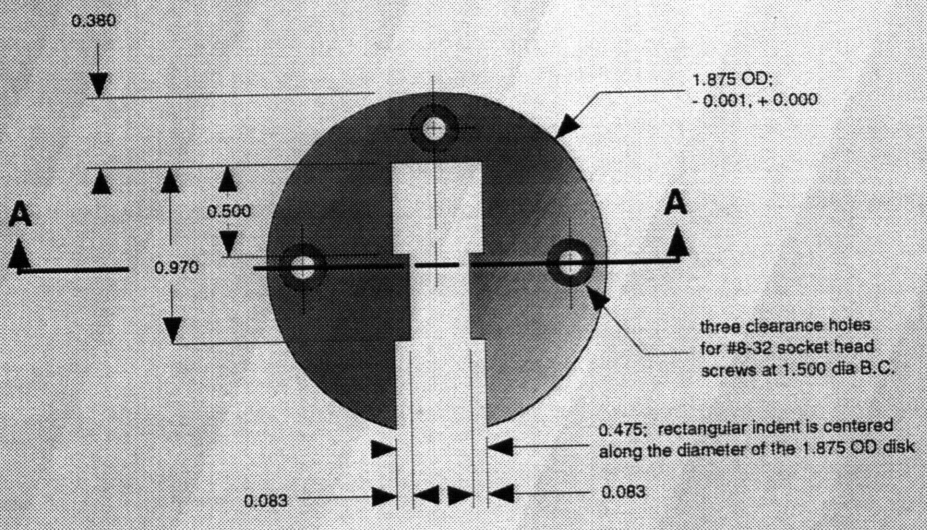
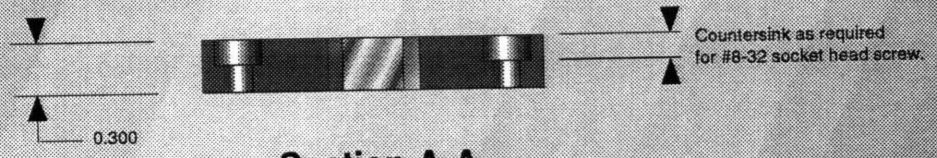
Plan 4.G.



Bottom view



Section A-A

Assembly Notes:

(1) Machine the anchor plate, as indicated in the drawings above.

(2) Weld anchor plate to the lower end of the larger arm of the 3-3/8" to 1-1/3" Conflat flange reducing cross. The anchor plate must be positioned so that its outside face is 0.200 from the extreme outside face of the lower 3-3/8" Conflat flange on the reducing cross. The anchor plate must be rotated so that the long axis of the rectangular-shaped indent in the disk is parallel to the axis of the small arms of the reducing cross.

(3) Screw the reducing cross shell guide to the guide plate.

Project title:	**Powder Pipet**
Part designation:	**Reducing cross guide anchor plate**
Material:	**Stainless steel**
Number of parts:	**1 assembly**
Tolerance:	**+,- 0.005" (unspec.)**
Part design by:	**Brian Norio Hubert**
Drawing date:	**November 28, 1995**

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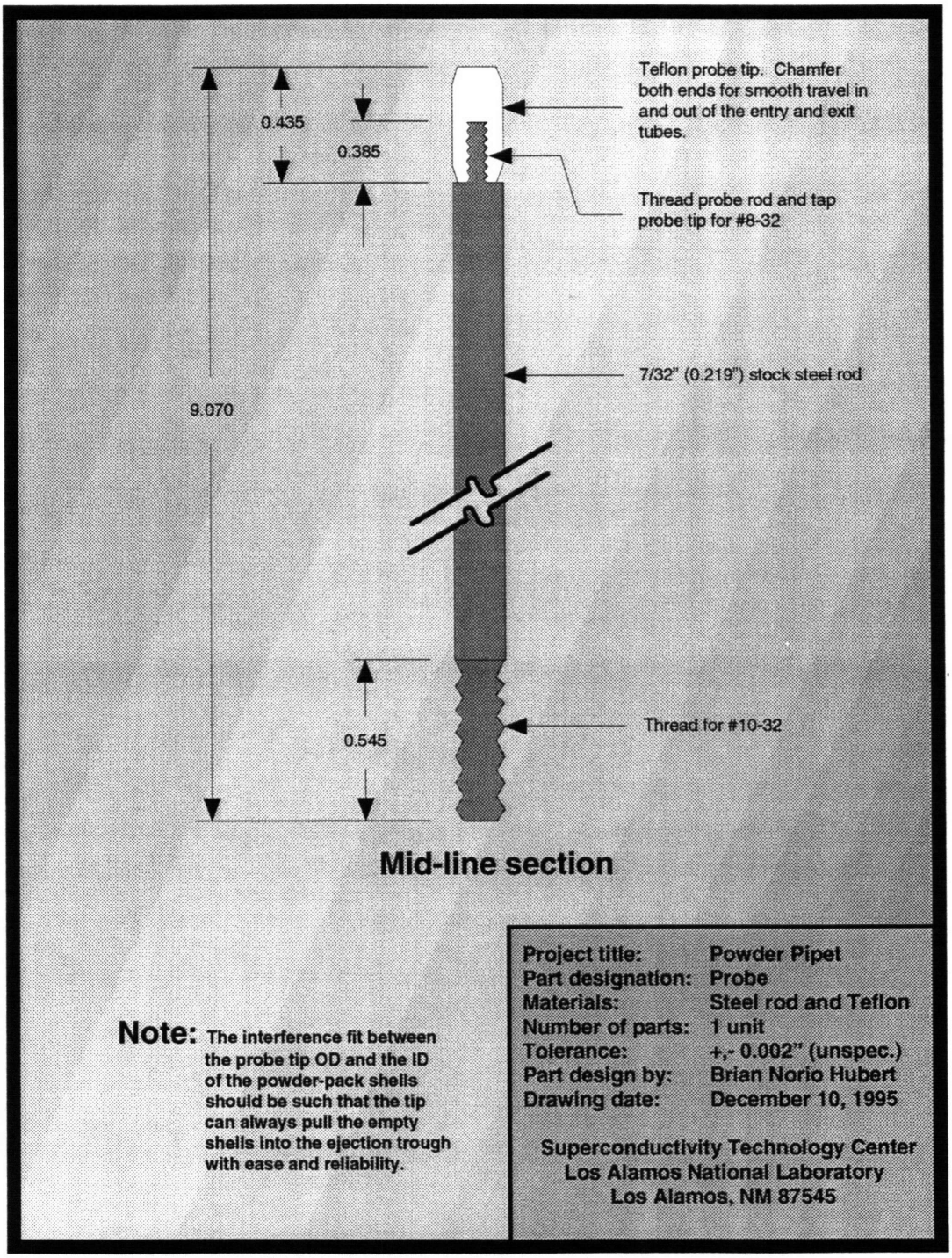
Plan 4.H.


0.435
0.385
9.070
0.545
Teflon probe tip. Chamfer both ends for smooth travel in and out of the entry and exit tubes.
Thread probe rod and tap probe tip for #8-32
7/32" (0.219") stock steel rod
Thread for #10-32
Mid-line section
Note: The interference fit between the probe tip OD and the ID of the powder-pack shells should be such that the tip can always pull the empty shells into the ejection trough with ease and reliability.
Project title: Powder Pipet
Part designation: Probe
Materials: Steel rod and Teflon
Number of parts: 1 unit
Tolerance: +,- 0.002" (unspec.)
Part design by: Brian Norio Hubert
Drawing date: December 10, 1995
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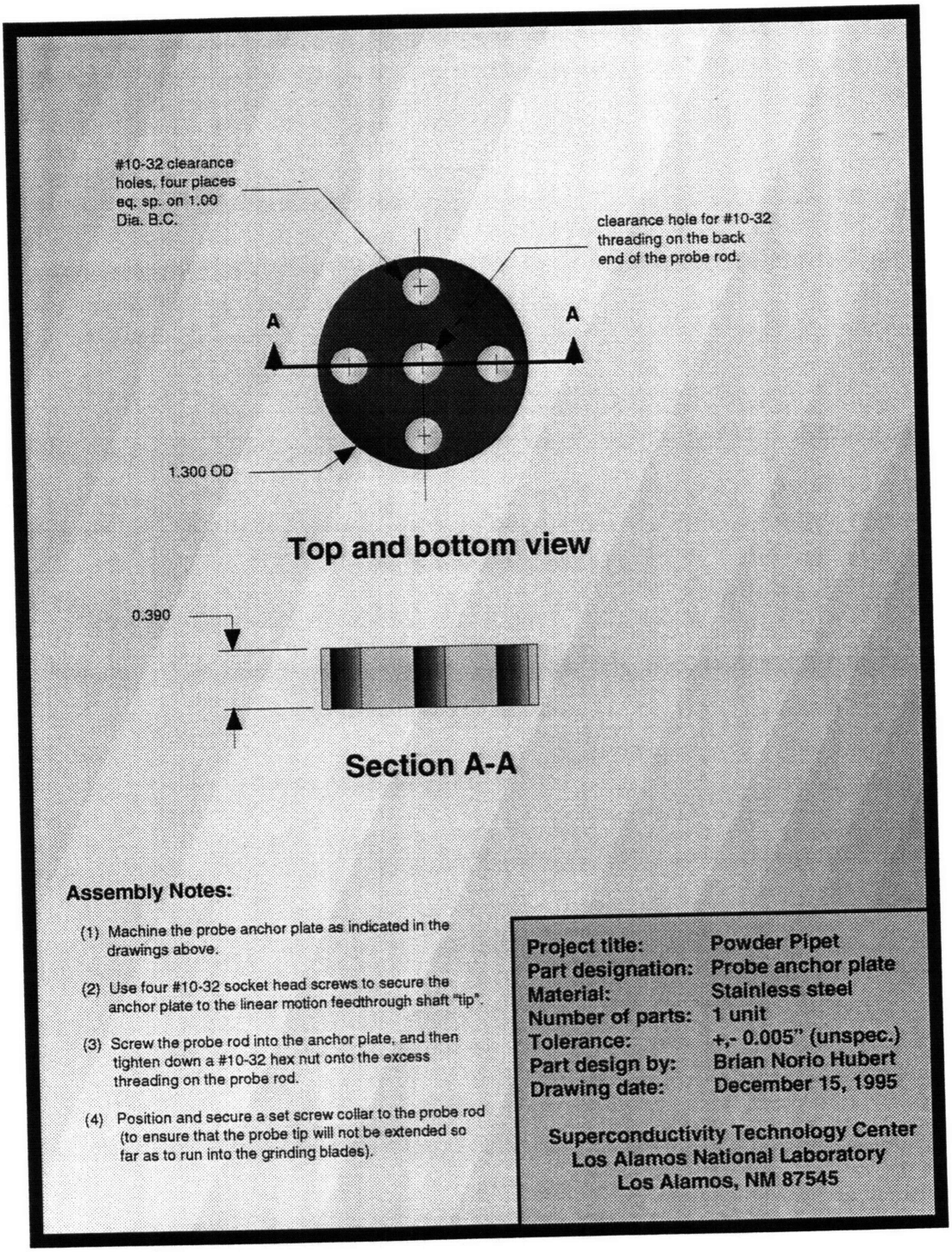
Plan 4.I.


#10-32 clearance holes, four places eq. sp. on 1.00 Dia. B.C.
clearance hole for #10-32 threading on the back end of the probe rod.
A
A
1.300 OD
Top and bottom view
0.390
Section A-A
Assembly Notes:
(1) Machine the probe anchor plate as indicated in the drawings above.
(2) Use four #10-32 socket head screws to secure the anchor plate to the linear motion feedthrough shaft "tip".
(3) Screw the probe rod into the anchor plate, and then tighten down a #10-32 hex nut onto the excess threading on the probe rod.
(4) Position and secure a set screw collar to the probe rod (to ensure that the probe tip will not be extended so far as to run into the grinding blades).
Project title: Powder Pipet
Part designation: Probe anchor plate
Material: Stainless steel
Number of parts: 1 unit
Tolerance: +,- 0.005" (unspec.)
Part design by: Brian Norio Hubert
Drawing date: December 15, 1995
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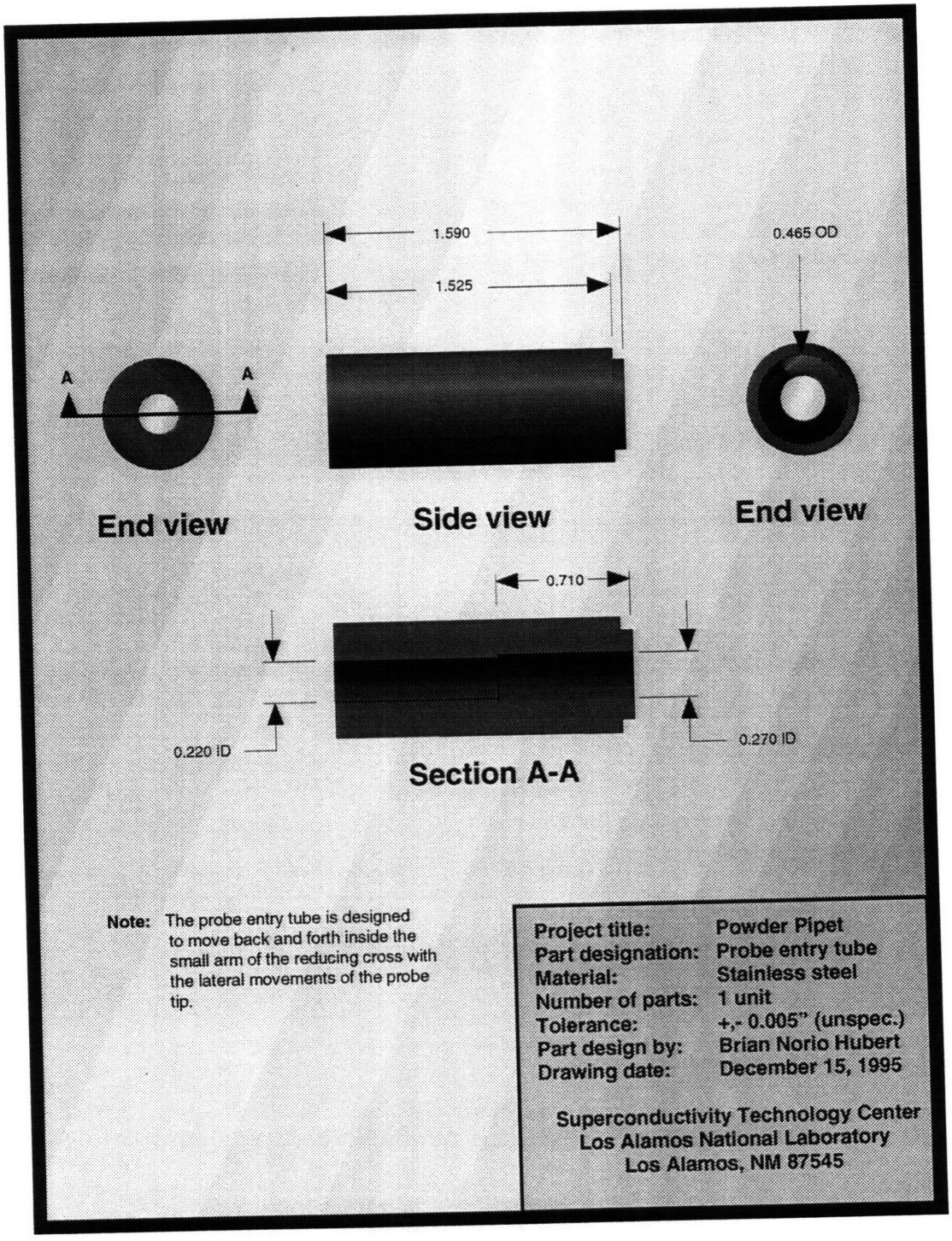
Plan 4.J.



Note: The probe entry tube is designed to move back and forth inside the small arm of the reducing cross with the lateral movements of the probe tip.

Project title:	**Powder Pipet**
Part designation:	**Probe entry tube**
Material:	**Stainless steel**
Number of parts:	**1 unit**
Tolerance:	**+,- 0.005" (unspec.)**
Part design by:	**Brian Norio Hubert**
Drawing date:	**December 15, 1995**

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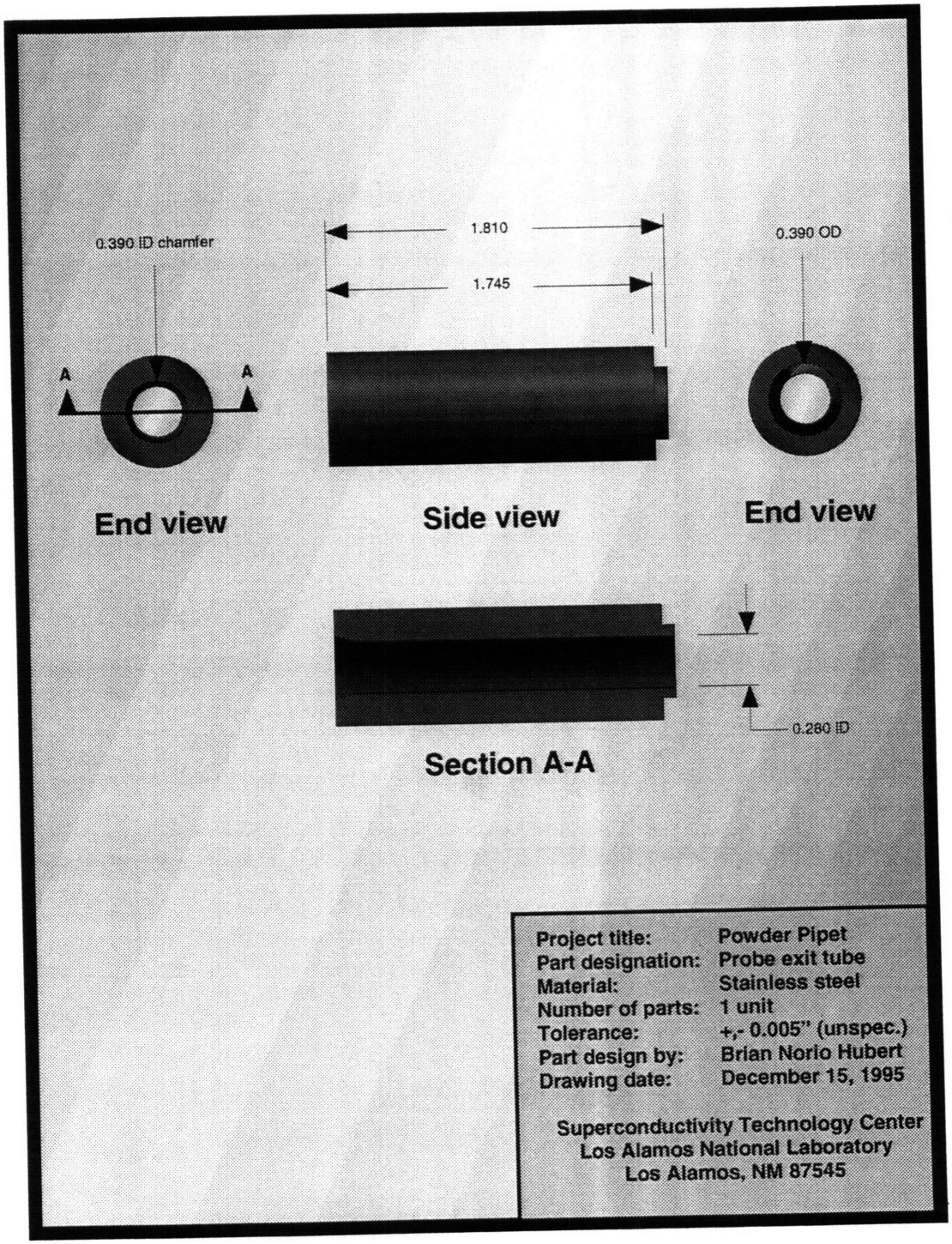
Plan 4.K.


0.390 ID chamfer
A
A
End view
1.810
1.745
Side view
0.390 OD
End view
0.280 ID
Section A-A
Project title: Powder Pipet
Part designation: Probe exit tube
Material: Stainless steel
Number of parts: 1 unit
Tolerance: +,- 0.005" (unspec.)
Part design by: Brian Norio Hubert
Drawing date: December 15, 1995
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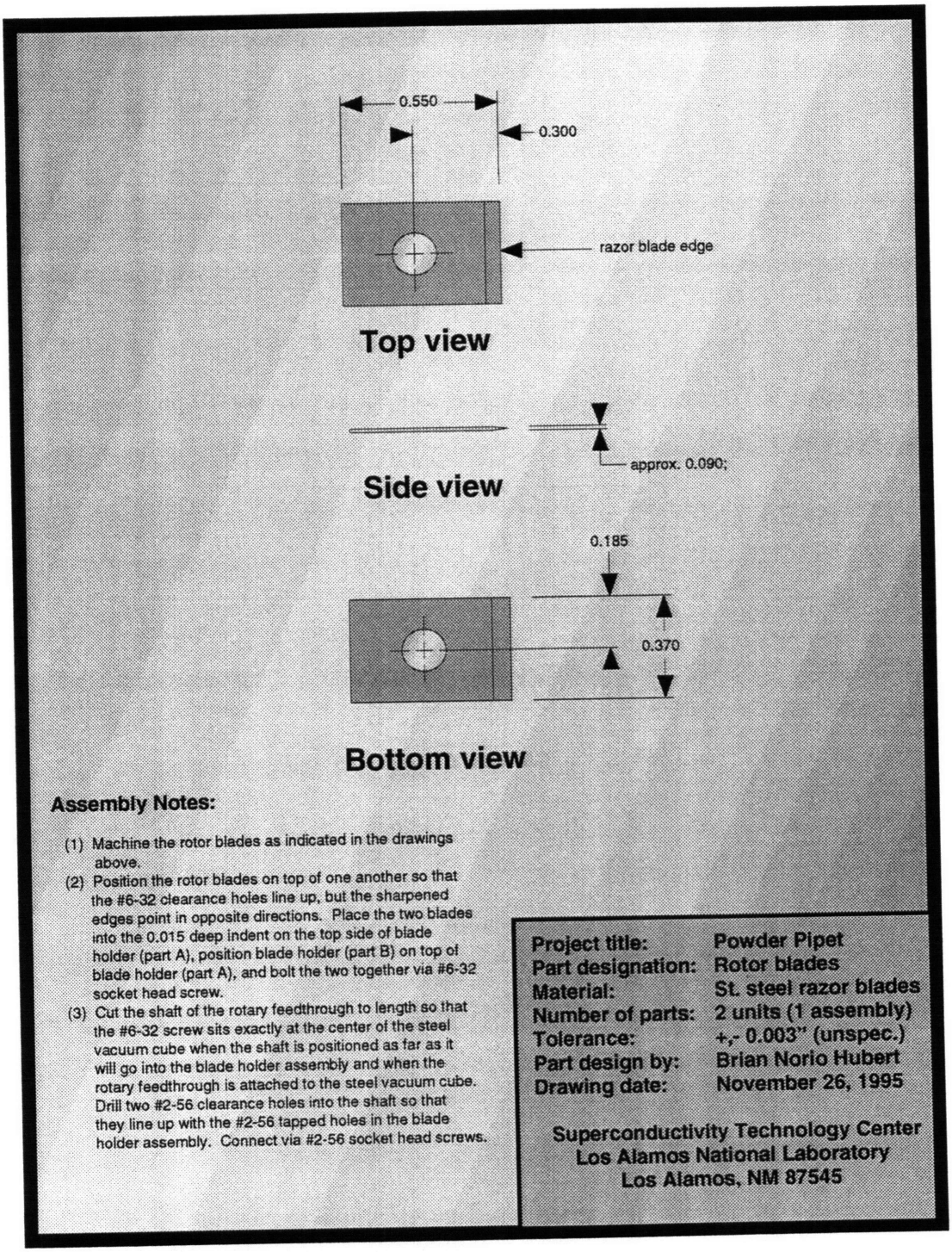
Plan 4.L.



Assembly Notes:

(1) Machine the rotor blades as indicated in the drawings above.
(2) Position the rotor blades on top of one another so that the #6-32 clearance holes line up, but the sharpened edges point in opposite directions. Place the two blades into the 0.015 deep indent on the top side of blade holder (part A), position blade holder (part B) on top of blade holder (part A), and bolt the two together via #6-32 socket head screw.
(3) Cut the shaft of the rotary feedthrough to length so that the #6-32 screw sits exactly at the center of the steel vacuum cube when the shaft is positioned as far as it will go into the blade holder assembly and when the rotary feedthrough is attached to the steel vacuum cube. Drill two #2-56 clearance holes into the shaft so that they line up with the #2-56 tapped holes in the blade holder assembly. Connect via #2-56 socket head screws.

Project title:	**Powder Pipet**
Part designation:	**Rotor blades**
Material:	**St. steel razor blades**
Number of parts:	**2 units (1 assembly)**
Tolerance:	**+,- 0.003" (unspec.)**
Part design by:	**Brian Norio Hubert**
Drawing date:	**November 26, 1995**

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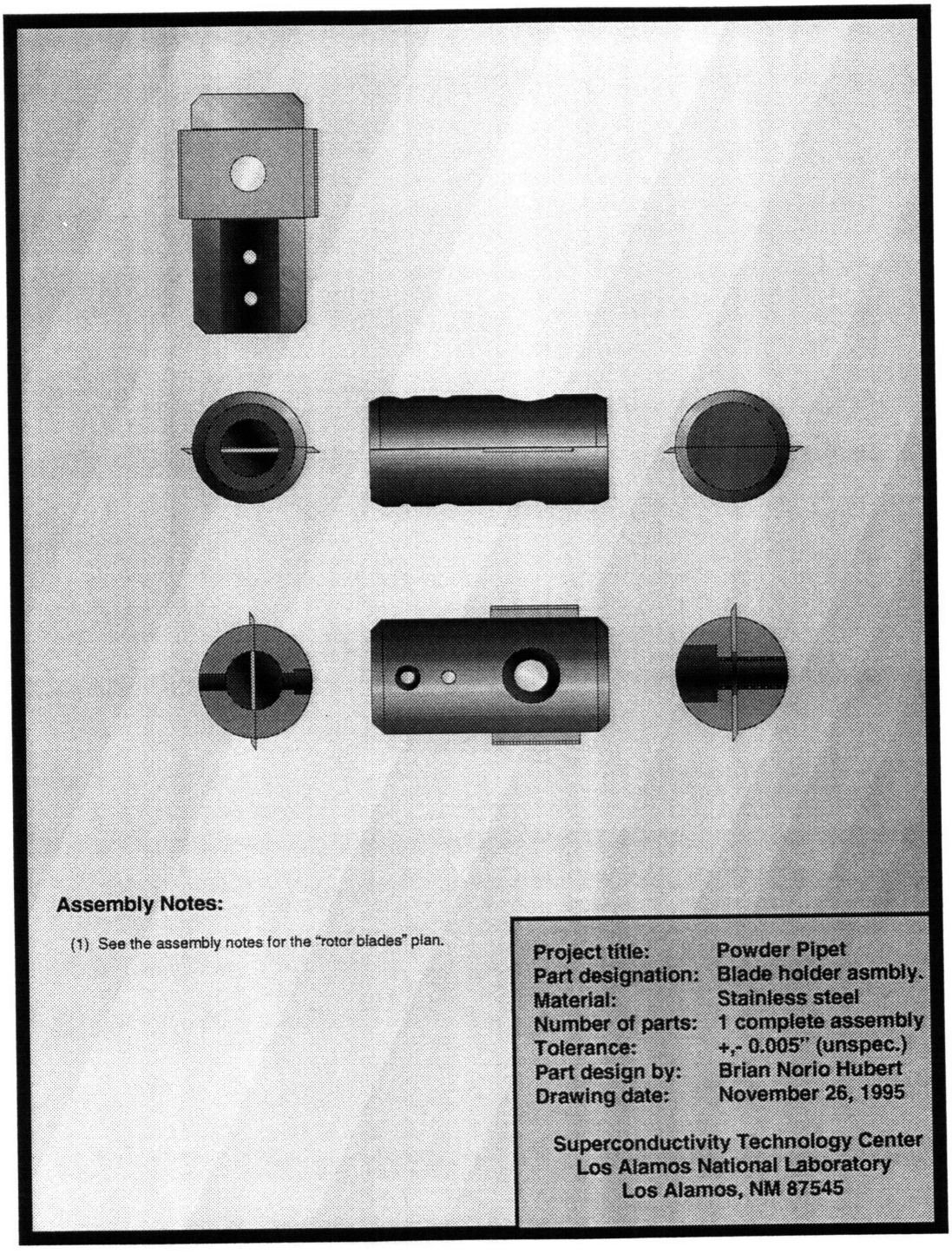
Plan 4.M.



Assembly Notes:

(1) See the assembly notes for the "rotor blades" plan.

Project title:	**Powder Pipet**
Part designation:	**Blade holder asmbly.**
Material:	**Stainless steel**
Number of parts:	**1 complete assembly**
Tolerance:	**+,- 0.005" (unspec.)**
Part design by:	**Brian Norio Hubert**
Drawing date:	**November 26, 1995**

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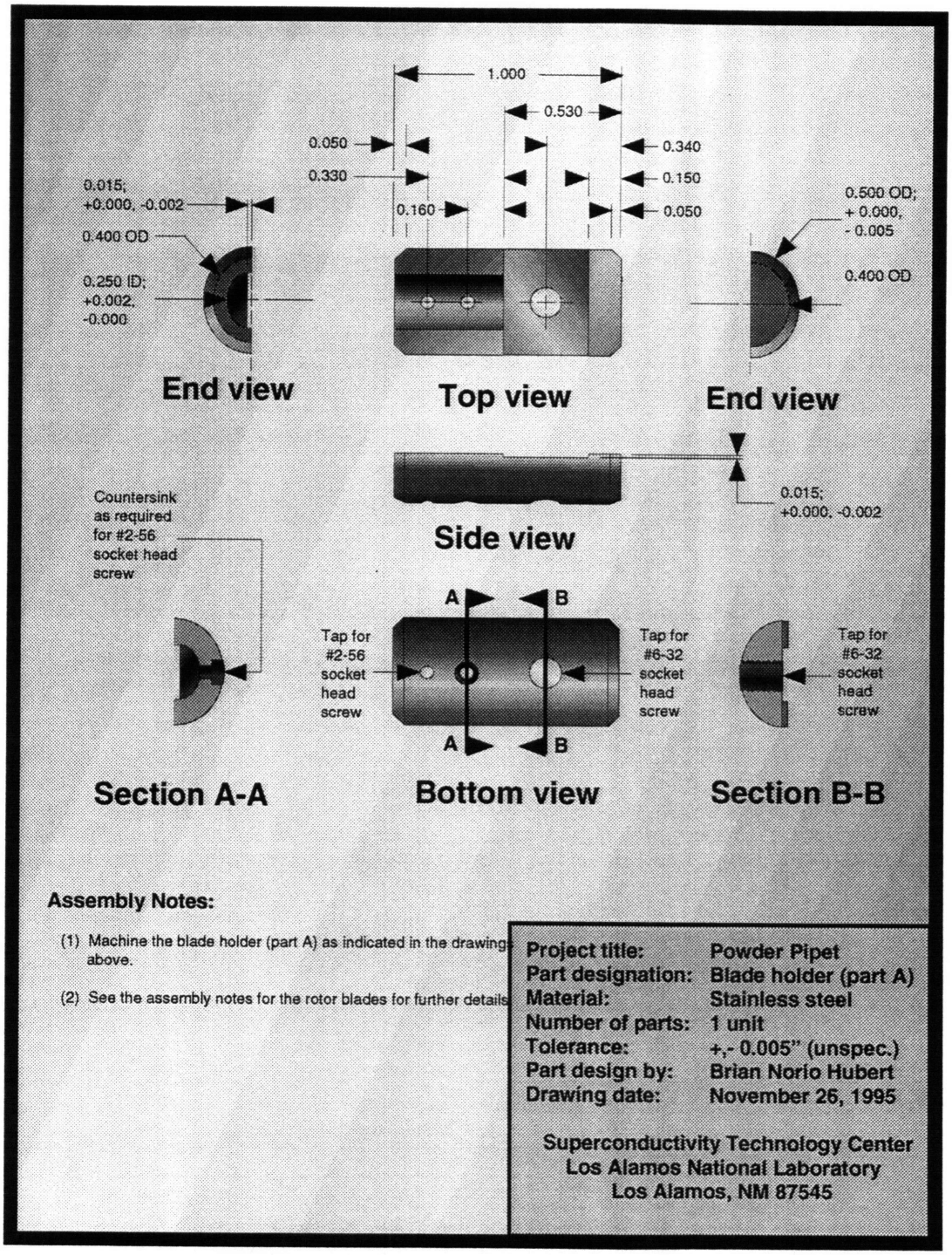
Plan 4.N.



Assembly Notes:

(1) Machine the blade holder (part A) as indicated in the drawing above.

(2) See the assembly notes for the rotor blades for further details.

Project title:	**Powder Pipet**
Part designation:	**Blade holder (part A)**
Material:	**Stainless steel**
Number of parts:	**1 unit**
Tolerance:	**+,- 0.005" (unspec.)**
Part design by:	**Brian Norio Hubert**
Drawing date:	**November 26, 1995**

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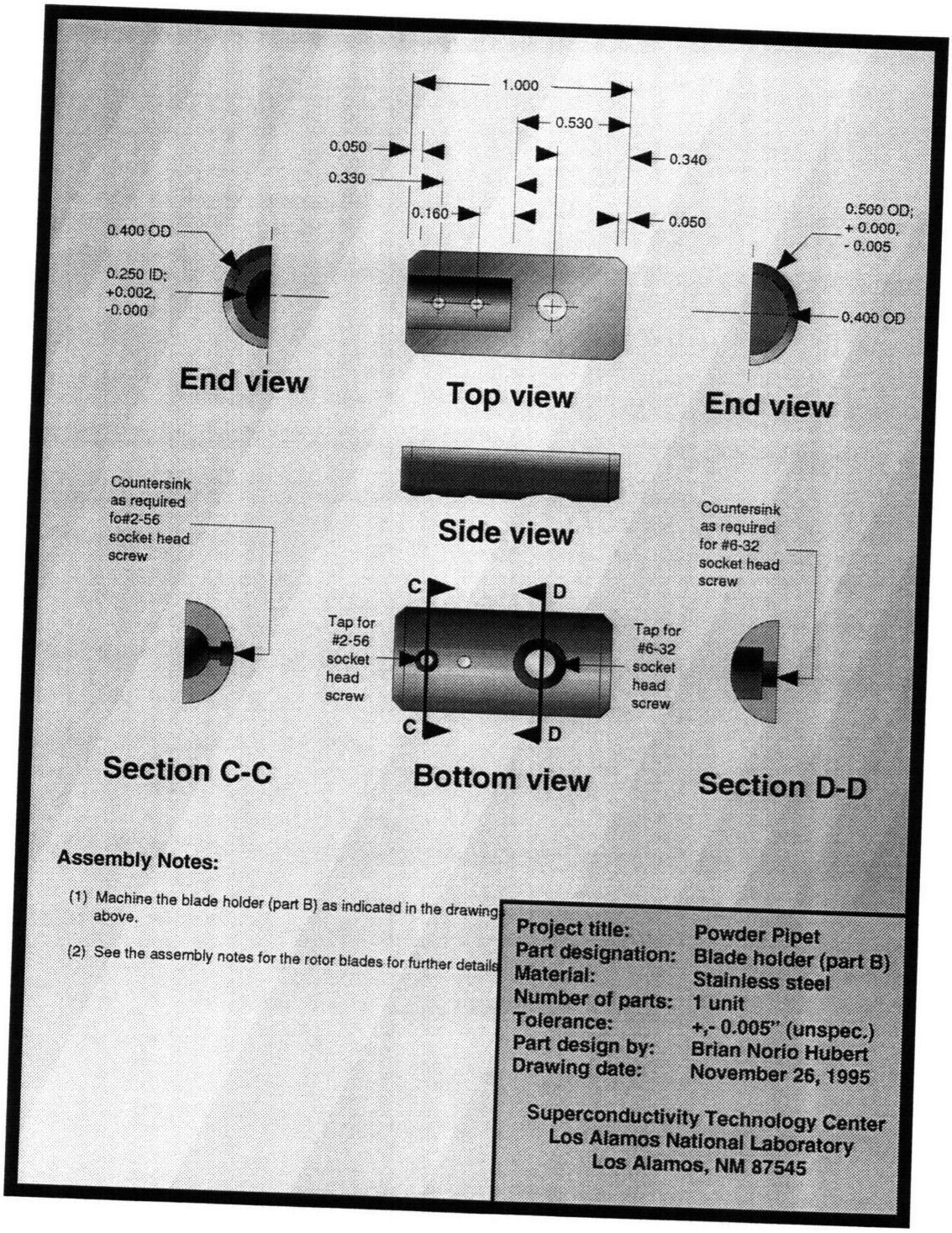
Plan 4.O.



Assembly Notes:

(1) Machine the blade holder (part B) as indicated in the drawing above.

(2) See the assembly notes for the rotor blades for further details

Project title:	**Powder Pipet**
Part designation:	**Blade holder (part B)**
Material:	**Stainless steel**
Number of parts:	**1 unit**
Tolerance:	**+,- 0.005" (unspec.)**
Part design by:	**Brian Norio Hubert**
Drawing date:	**November 26, 1995**

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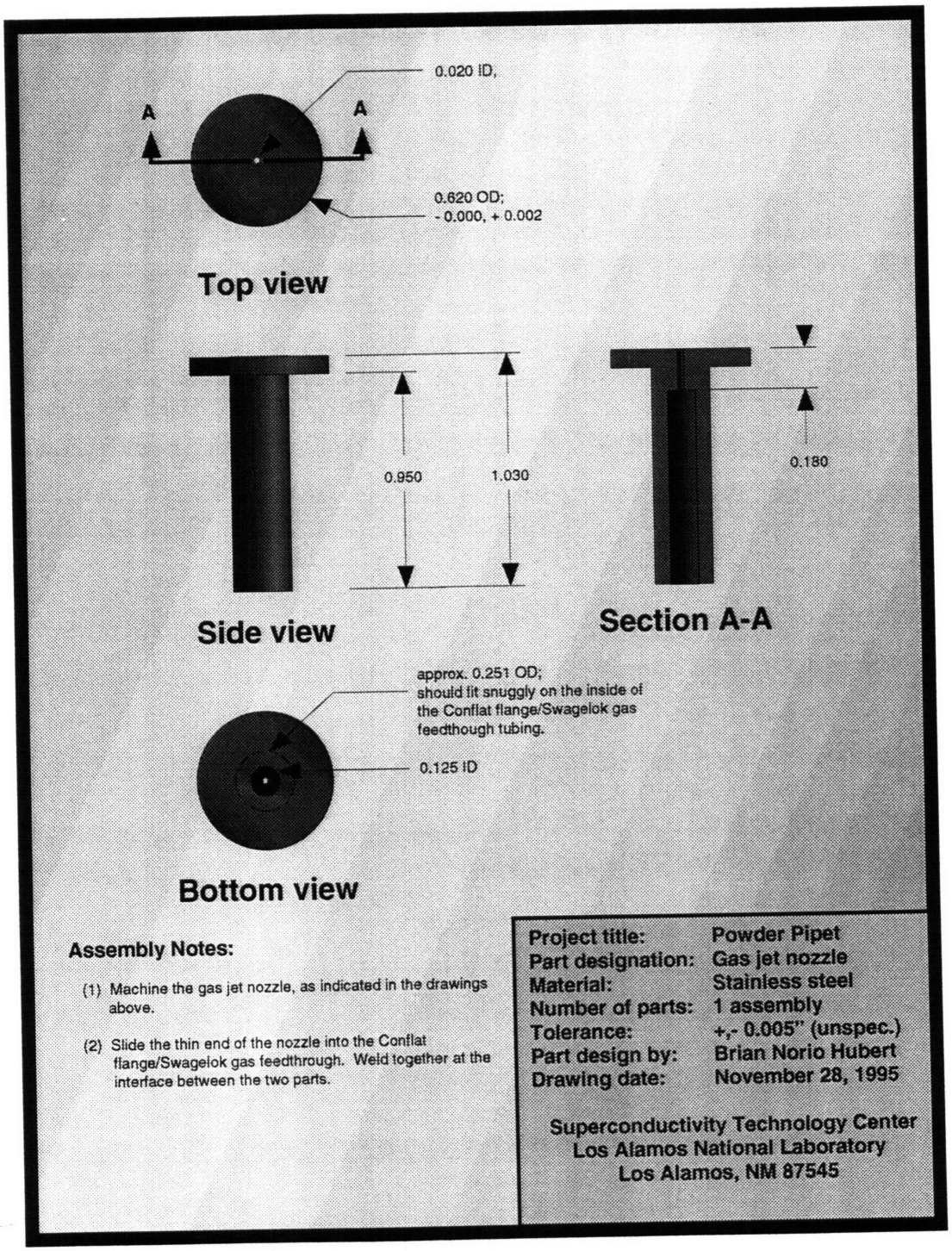
Plan 4.P.


0.020 ID,
A
A
0.620 OD;
- 0.000, + 0.002
Top view
0.950
1.030
0.180
Side view
Section A-A
approx. 0.251 OD;
should fit snuggly on the inside of
the Conflat flange/Swagelok gas
feedthough tubing.
0.125 ID
Bottom view
Assembly Notes:
(1) Machine the gas jet nozzle, as indicated in the drawings above.
(2) Slide the thin end of the nozzle into the Conflat flange/Swagelok gas feedthrough. Weld together at the interface between the two parts.
Project title: Powder Pipet
Part designation: Gas jet nozzle
Material: Stainless steel
Number of parts: 1 assembly
Tolerance: +,- 0.005" (unspec.)
Part design by: Brian Norio Hubert
Drawing date: November 28, 1995
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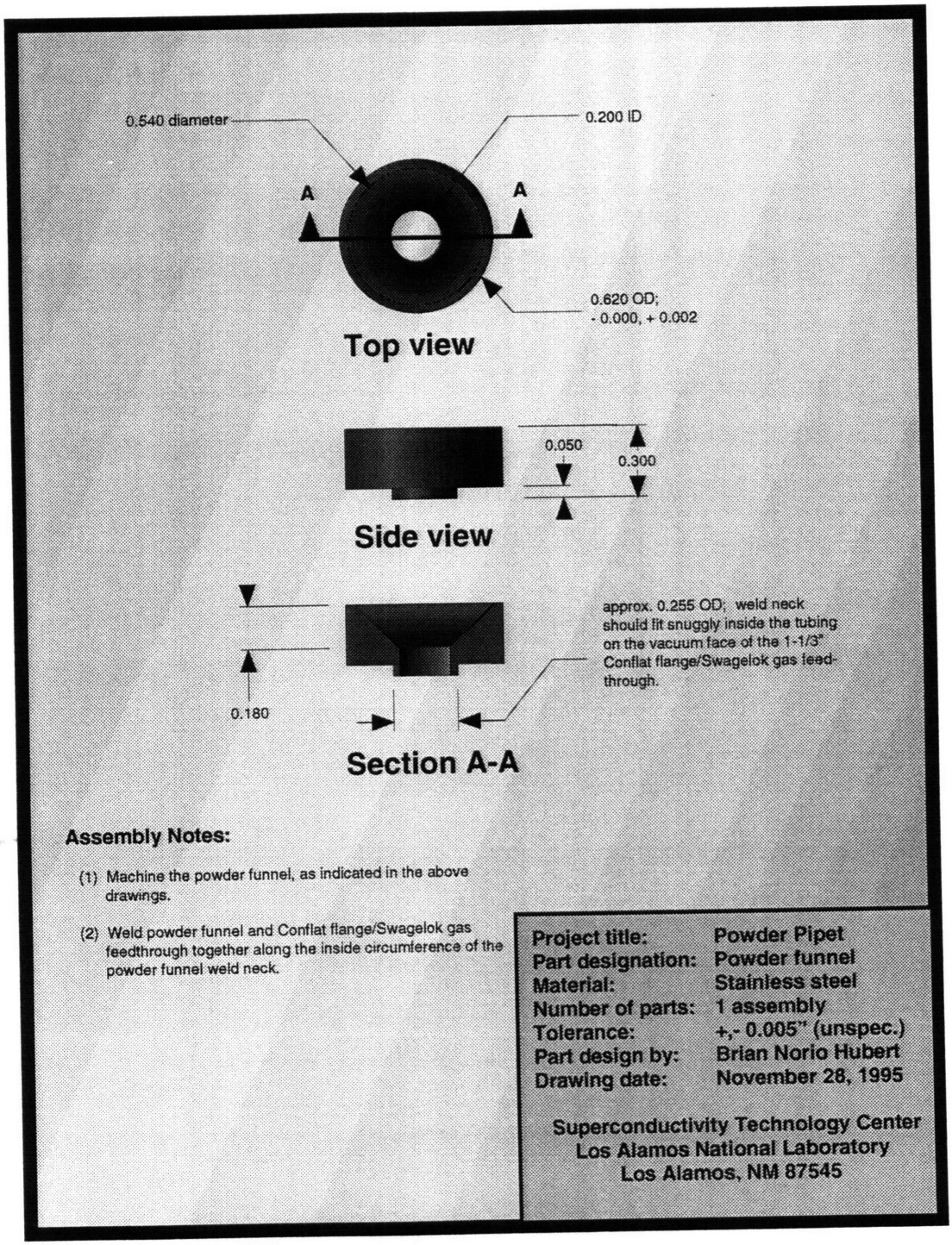
Los Alamos, NM 87545

Plan 4.Q.


0.540 diameter
0.200 ID
A
A
0.620 OD;
- 0.000, + 0.002
Top view
0.050
0.300
Side view
approx. 0.255 OD; weld neck should fit snuggly inside the tubing on the vacuum face of the 1-1/3" Conflat flange/Swagelok gas feed-through.
0.180
Section A-A
Assembly Notes:
(1) Machine the powder funnel, as indicated in the above drawings.
(2) Weld powder funnel and Conflat flange/Swagelok gas feedthrough together along the inside circumference of the powder funnel weld neck.
Project title: Powder Pipet
Part designation: Powder funnel
Material: Stainless steel
Number of parts: 1 assembly
Tolerance: +,- 0.005" (unspec.)
Part design by: Brian Norio Hubert
Drawing date: November 28, 1995
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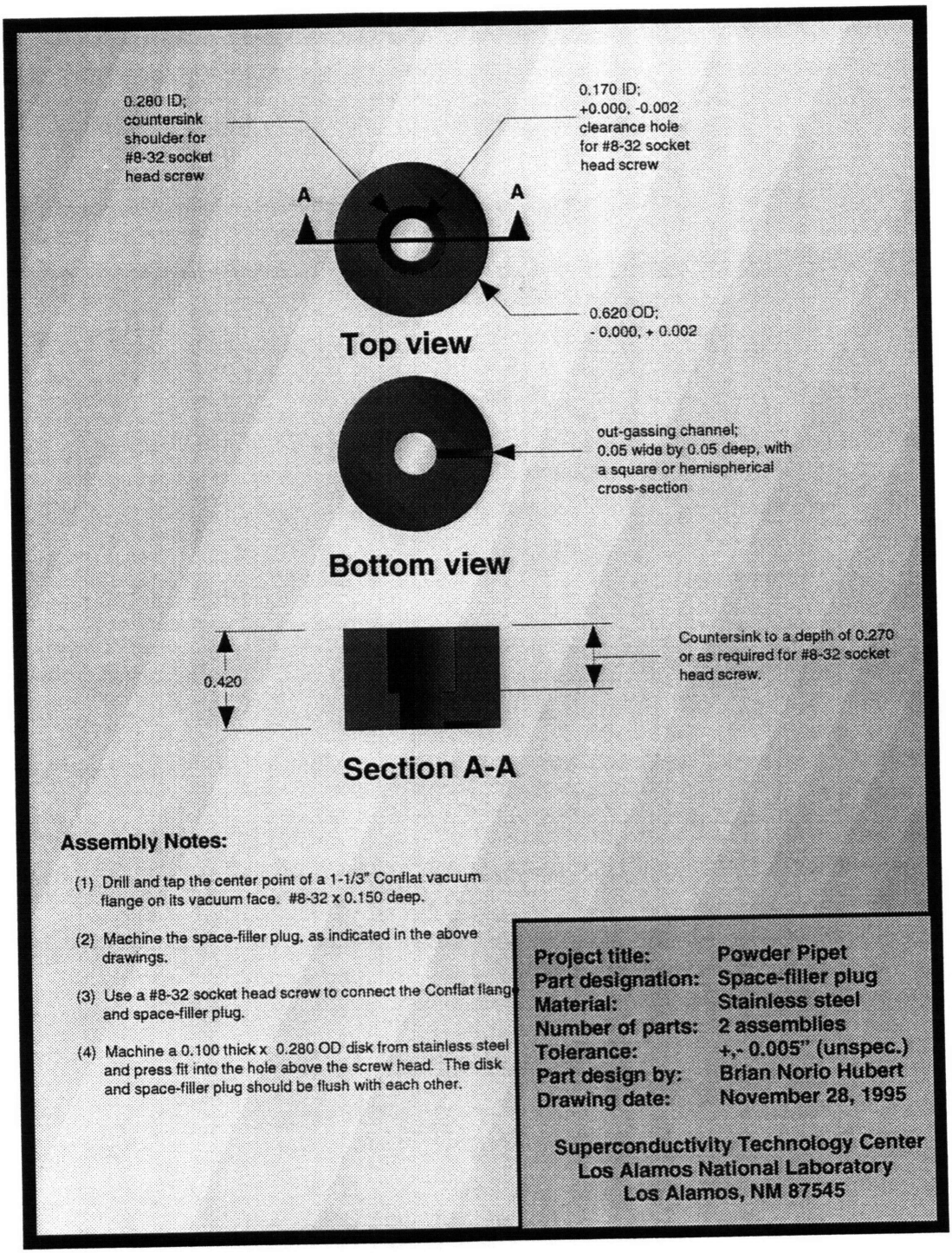
Plan 4.R.


0.280 ID;
countersink
shoulder for
#8-32 socket
head screw
0.170 ID;
+0.000, -0.002
clearance hole
for #8-32 socket
head screw
A
A
0.620 OD;
- 0.000, + 0.002
Top view
out-gassing channel;
0.05 wide by 0.05 deep, with
a square or hemispherical
cross-section
Bottom view
0.420
Countersink to a depth of 0.270
or as required for #8-32 socket
head screw.
Section A-A
Assembly Notes:
(1) Drill and tap the center point of a 1-1/3" Conflat vacuum flange on its vacuum face. #8-32 x 0.150 deep.
(2) Machine the space-filler plug, as indicated in the above drawings.
(3) Use a #8-32 socket head screw to connect the Conflat flange and space-filler plug.
(4) Machine a 0.100 thick x 0.280 OD disk from stainless steel and press fit into the hole above the screw head. The disk and space-filler plug should be flush with each other.
Project title: Powder Pipet
Part designation: Space-filler plug
Material: Stainless steel
Number of parts: 2 assemblies
Tolerance: +,- 0.005" (unspec.)
Part design by: Brian Norio Hubert
Drawing date: November 28, 1995
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5 ConBrio vs. 'ideal': system comparison

The attributes and characteristics of the ConBrio deposition system presented in Chapter 4 will now be compared to the hypothetical 'ideal' system proposed in Chapter 3.

5.1 Source materials

Ideal

An ideal deposition system should be capable of processing non-fluorinated β-diketonate metalorganic compounds of yttrium, barium, and copper. It is hoped that more stable and volatile precursor substances will be discovered in the near future, but at the present time, β-diketonates are the most reliable and cost-effective sources that the field has to offer.

Because solvents can have a detrimental effect on superconductor current densities and transition temperatures, an ideal deposition system should employ only solid-source techniques to enhance precursor volatility and facilitate the transport of precursor materials to the substrate.

ConBrio

The ConBrio system is capable of processing Y, Ba, and Cu β-diketonate precursor materials, and therefore meets the requirements of the ideal system. In addition, ConBrio can process and grow a variety of electro-optic materials including $LiNbO_3$, $Sr_xBa_{1-x}Nb_2O_6$, and $KNbO_3$. Any material that can be deposited and grown using a Hiskes-style or bubbler solid-source technique, can also be grown by the ConBrio system.

The ConBrio system requires no solvents for precursor delivery, and keeps source materials in the solid state until the moment of vaporization. Unlike the area-*minimizing* Hiskes and bubbler delivery mechanisms that confine precursor materials to cartridges and crucibles, the Powder Pipet *maximizes* precursor surface area by generating millions of submicron powder particles per minute. Particulates of such small size exhibit enhanced volatility during the vaporization process. Due to this increase in volatility, ConBrio will be capable of supporting high deposition rates.

5.2 Control of source material release

Ideal

An ideal feeder/delivery mechanism should initiate the release of source materials into a carrier gas stream by employing only well-understood mechanical processes. As discussed in Chapter 3, vaporization and vibratory delivery processes --- like those found in the Hiskes, Lackey, and Schulte systems --- are too complex and difficult to control. An ideal mechanism would also exhibit the following two characteristics: (1) independent composition and mass flow control variables regulated by a single set of input signals; and (2) real-time control (i.e. control with little if any delay) of composition via gas stoichiometry analyzer feedback loop.

ConBrio

The Powder Pipet controls precursor mass flow with one simple mechanical process --- linear motion of the probe pushing on the back end of the precursor powder pack. Mass flow rate can be increased by increasing probe velocity, and vice versa. The Hiskes delivery system employs a similar linear motion mechanism to control precursor mass flow rate. However, the true advantage of the Powder Pipet lies in the means by which material becomes disassociated from the main body of the precursor powder pack. As the probe pushes the powder pack into the blades of the high-speed grinding rotor, sub-micron particulates of precursor material are scraped off the exposed tip of the powder pack. In contrast, the Hiskes system relies on thermal processes for precursor material disassociation. As shown by Meng *et al.*[1], the molecular interactions occurring in the 'melt wedge' zone at the tip of the powder cartridge are exceedingly complex and difficult to control and model.

The Powder Pipet can decrease particle size by increasing grinder rotor speed, and vice versa. However, because small powder particles are preferred over larger ones, rotor speed will generally be fixed at the highest speed available. Once a rotational speed has been established, it ceases to be an active control variable. Therefore, during normal operation, the Powder Pipet has only one control variable --- linear velocity of the probe. This variable regulates precursor flow to downstream processes. Velocity control of the probe is a mechanical problem that is easily solved by any sufficiently accurate linear mechanism. When only one probe is being used, composition is controlled by the pre-mixture of powder species packed into the shells. If multiple probes are available, as in the case when multiple vertical and horizontal tube assemblies are attached to a common grinder assembly, mass flow of each of the Y, Ba, and Cu precursor species can be controlled independently. In this case, the velocities of the probes relative to one another determines the composition of the powders being disseminated into the gas stream.

In summary, the velocity of each probe determines precursor flow rate, and the *relative* velocities of the probes (if more than one probe, and thus more than one species of precursor, is being used) determines the composition. Therefore, like an ideal delivery/feeder mechanism, the Powder Pipet uses *one* set of control variables --- probe velocities --- to regulate composition *and* precursor delivery rate *independently.*

1. G. Meng *et al.* Appl. Phys. Letters, Vol. 63, No. 14, 1993.

Precursor vapor density and composition in the carrier gas should remain nearly constant over the entire duration of the deposition run. Sudden increases or dips in vapor phase density are undesirable, and should be corrected as soon as possible. Likewise, stoichiometry (the balance between the various precursor species within the vapor phase) should also be kept within parameters. A gas stoichiometry analyzer with a feedback loop to the linear feedthrough controller(s) can be attached to the gas line just downstream from the vaporizer to monitor vapor density and composition. Because the Powder Pipet generates powder particles on demand just a split second before they are sublimed in the vaporizer, errors in density or composition can be corrected by this feedback loop almost instantly. In contrast, liquid-source and powder-source delivery systems require mixing reservoirs and exhibit long time constants. Depending on system configuration, many seconds or even minutes can pass before an error can be corrected.

5.3 Thermal considerations

Ideal

An ideal YBCO deposition system should *not* thermally degrade precursor materials or generate undesirable thermal gradients in excessively long gas lines. An ideal deposition system should use a susceptor with a uniform radiation pattern and a capability for compensating for substrate absorptance changes.

ConBrio

Because the Powder Pipet feeder is thermally isolated from the vaporizer, the ConBrio system does not in any way subject precursor materials to *premature* thermal degradation. This isolation is possible because the Powder Pipet does not depend on the vaporization of the precursor powder pack to initiate mass flow to downstream processes. The juxtaposition problems of the Hiskes system are no more. In theory, the Powder Pipet and the vaporizer can be separated by a gas line of arbitrary length.

Particulates generated by the Powder Pipet endure residence times of less than a half-second while traveling through the vaporizer and a very short (< 3") heated line to the deposition chamber. At the present time, the author has not yet attempted to optimize the radiation patterns or absorptance compensatory characteristics of the susceptor.

5.4 Carrier and processing gases

Ideal

An ideal deposition system should isolate all deposition processes from outside air at all times. Ar or He carrier gasses should be supplemented by amine vapors, and should be transported to the substrate in a constant state of laminar flow. N_2O or a mixture of N_2O and O_2 should serve as the primary oxygen source. And finally, the deposition chamber should include geometric features and substrate alignments that tend to thin down boundary layers and improve the uniformity of vapor pressures across the entire substrate surface.

ConBrio

The entire ConBrio system is compact enough to fit inside a medium-size glove box, and therefore can be isolated from outside air. Carrier gases consist of a mixture of Ar or He gas and amine vapors of NH_3, and $N(CH)_3$ at low total pressure. This combination should reduce the degree of thermal degradation at the

deposition zone and also increase critical transition temperatures. N_2O is used as the primary oxygen source, which should have the effect of reducing deposition temperature. And lastly, substrates within the deposition chamber are aligned parallel to the flow of incoming gas, and vapor-laden gases pass through a diffusion baffeling just before reaching the substrate.

5.5 Economic considerations

Ideal

High product throughput and high product quality are the two primary economic characteristics of an ideal YBCO deposition system. Such a system would provide a commercially viable alternative to current deposition systems.

ConBrio

The ConBrio system was designed to produce a consistently superior superconducting product at a significantly reduced cost. The apparatus design is very simple, and only low-cost processes are employed in its operation. No high-powered lasers, reservoirs, supersonic sprayers, liquid pumping mechanisms, or other exotic and expensive devices are required. For example, the Powder Pipet feeder sub-system is constructed from 95% stock vacuum system components by weight. The few custom parts that are required, are easily machined. Because the Powder Pipet exhibits a highly modular design, it can simultaneously process any number of precursor species with the attachment of additional vertical tube and horizontal tube assemblies. With the addition of a pair of ball valves, the feeder can support continuous process deposition runs for the production of very long lengths of superconducting wires and tapes.

The ConBrio deposition system is inherently robust, making maintenance economical. Because the entire apparatus contains only three moving parts --- the probe, the powder grinder, and a vacuum pump --- the number of failure modes has been minimized. The ConBrio system has only one major control parameter --- probe velocity. This makes the system simple and inexpensive to operate and monitor. And because this control parameter can be regulated with extreme precision (especially if piezoelectric linear motors are used to drive the probe), large of amounts of costly precursor materials do not have to be released into the carrier gas stream to compensate for control deficiencies.

6 Conclusion

In this work, the author has subjected a number of YBCO superconductor deposition systems developed by various laboratories to a critical review and analysis. Deficiencies in the design of these deposition processes were identified. Most of these deficiencies have resulted in either poor end-product performance or unlikely commercial viability. For example: pulsed laser deposition systems are capable of producing very high quality superconducting films, but their deposition rates are far too slow to be commercially viable; liquid-source MOCVD systems can be precisely controlled, but the solvents they require tend to kill superconducting oxides; and solid-source MOCVD systems suffer from imprecise process control, thermal degradation of precursor materials, or both. A simple and affordable alternative MOCVD system, called ConBrio, has been proposed as an enticing alternative to existing deposition systems. In summary, the author makes the following claims on behalf of the ConBrio MOCVD system:

- a deposition system that is classified as a solid-source metalorganic chemical vapor deposition (MOCVD) system
- a deposition system that consists of three main parts --- a precursor feeder device called the Powder Pipet, a vaporizer, and a deposition chamber with a susceptor-heated deposition zone
- a deposition system that is capable of producing high quality YBCO superconducting films from Y, Ba, and Cu β-diketonate precursor materials, and can also deposit a variety of other materials including organometallics, electro-optical materials, and semiconductors
- a deposition system that should be capable of supporting very high deposition rates, and yet still control deposition processes with a high degree of precision
- a deposition system that, in theory, should not subject source materials to any thermal degradation, thanks to thermal isolation of the feeder device from the vaporizer
- a deposition system that uses carrier gases supplemented by amine vapors at low total pressure, and also uses N_2O as

the primary oxygen source, to reduce deposition temperature, reduce the degree of thermal degradation at the deposition zone, and increase critical transition temperature

- a deposition system that can be constructed primarily from low-cost stock components generally available from vacuum components vendors

- a source material feeder device, the Powder Pipet, that is capable of supporting long-term continuous process depositions without breaking system vacuum conditions

- a source material feeder device that employs only simple mechanical processes (i.e. linear and rotational motion) for the dissemination of precursor materials into the carrier gas stream

- a source material feeder device that maximizes precursor volatility by generating small-diameter particulates that, when taken together, exhibit immense surface area

- a source material feeder device that uses only horizontal linear motion to: (1) push a powder-pack of source material out of a hollow shell and into a grinding assembly; (2) retract and eject the emptied shell; and (3) position the next shell in the que for subsequent processing

- a source material feeder device that is capable of independently regulating both precursor mass flow rate and composition via probe linear velocity as the single control parameter

- a source material feeder device that employs only two moving parts: a probe (its linear velocity regulates source material mass flow rate) and a bladed grinding rotor (its rotational velocity regulates the size of generated particulates)

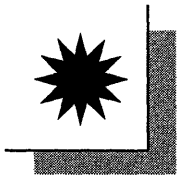
- a source material feeder device that is capable of processing multiple species of precursor materials simultaneously, thanks to modular design

- a source material feeder device whose "feed on demand" characteristics give it extremely short time constants for correction of precursor vapor density or compositional errors

- a source material feeder device that can be employed in any scientific field or commercial institution that requires the generation of very fine particulates over an extended period of time ---- for example: inhalation toxicology studies

- a vaporization unit that is capable of instantly vaporizing small-diameter particulates, thereby preventing the elongation of thermally degrading residence times

- a deposition chamber that contains geometric features that maintain laminar flow, thin down boundary layers, and improve vapor pressure uniformity across the substrate surface --- these features include a *very* short heated line between the vaporizer and the deposition chamber, a chamber entrance with gradually increasing diameter, diffusion baffeling, and alignment of the substrate parallel to the flow of incoming gases and source material vapors



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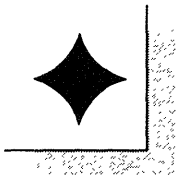

Suggested reading

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