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TOPICAL REPORT

EVALUATION OF METHODS FOR APPLICATION OF EPITAXIAL BUFFER AND SUPERCONDUCTOR LAYERS

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ABSTRACT

The recent achievements of critical currents exceeding million amperes per square centimeter at 77K in YBCO deposited over suitably textured substrate have stimulated interest in the potential applications of coated conductors at high temperatures and in high magnetic fields. Currently, ion-beam assisted deposition (IBAD), and rolling assisted bi-axially textured substrate (RABiTS), represent two available options for obtaining textured substrates. For applying suitable coatings of buffer and high temperature superconductor (HTS) material over textured substrates, several options are available which include sputtering, electron-beam evaporation, laser ablation, electrophoresis, chemical vapor deposition (including metal organics chemical vapor deposition), sol-gel, metal organics decomposition, electrodeposition and aerosol/spray pyrolysis. A commercial continuous long-length wire/tape manufacturing scheme developed out of any suitable combination of the above techniques would consist of operations involving preparation of the substrate and application of buffer, HTS and passivation/insulation materials and special treatment steps such as post-annealing. These operations can be effected by various process parameters that can be classified into chemistry, materials, engineering and environmental related parameters.

Under the DOE-sponsored program, to carry out an engineering evaluation, first, the process flow schemes were developed for various candidate options identifying the major operating steps, process conditions, and process streams. Next, to evaluate quantifiable parameters such as process severity (e.g. temperature and pressure), coating thickness and deposition rate for HTS material, achieved maximum J_c value (for films $>1\mu\text{m}$ thick) and cost of chemical and material utilization efficiency, the multi-attribute method was used to determine attributes/merits for various parameters and candidate options. To determine similar attribute values for the non-quantifiable parameters, a subjective evaluation was used. Results of the two evaluations were then combined to calculate the overall merit/utility of a given option using weighting factors. To evaluate the effect of arbitrarily determined weighting factors, a sensitivity analysis was carried out by using three different sets of weighting factors. In the end, the results of the overall utility/merit values calculated using different sets of weighting factors were utilized to determine the preliminary ranking among the candidate options.

As a result of this study, MOD, Sol-Gel, MOCVD, E-Beam and PLD options have been identified as the leading candidates for continuous, long-length processing of coated HTS conductors. However, there are several technical concerns related to each of these which need to be addressed first before a commercially viable option can be developed out of any one of them.

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1.0 Executive Summary

The recent achievements in a number of laboratories of critical currents in excess of 1.0×10^6 amp/cm² at 77K in YBCO deposited over suitably textured buffer/substrate composites have stimulated interest in the potential applications of coated conductors at high temperatures and high magnetic fields. As of today, two different approaches for obtaining the textured substrates have been identified. These are: Los Alamos National Laboratory's (LANL) ion-beam assisted deposition called IBAD, to obtain a highly textured yttria-stabilized zirconia (YSZ) buffer on nickel alloy strips, and Oak Ridge National Laboratory's (ORNL) rolling assisted, bi-axially textured substrate option called RABiTS.

Similarly, based on the published literature, the available options to form High Temperature Superconductor (HTS) films on metallic, semi-metallic or ceramic substrates can be divided into: physical methods, and non-physical or chemical methods. Under these two major groups, the schemes being proposed consist of:

- Sputtering
- Electron-Beam Evaporation
- Flash Evaporation
- Molecular Beam Epitaxy
- Laser Ablation
- Electrophoresis
- Chemical Vapor Deposition (Including Metal-Organic Chemical Vapor Deposition)
- Sol-Gel
- Metal-Organic Decomposition
- Electrodeposition, and
- Aerosol/Spray Pyrolysis

In general, a spool-to-spool or reel-to-reel type of continuous manufacturing scheme developed out of any of the above techniques, would consist of:

- Preparation of Substrate Material
- Preparation and Application of the Buffer Layer(s)
- Preparation and Application of the HTS Material and Required Post-Annealing, and
- Preparation and Application of the External Passivation/Insulation Layer

These operations would be affected by various process parameters which can be classified into: Chemistry and Material Related Parameters; and Engineering and Environmental Based Parameters.

Thus, one can see that for successful development of the coated conductors manufacturing process, an extensive review of the available options was necessary. Under the U. S. Department of Energy (DOE's) sponsorship, the University of Tennessee Space Institute (UTSI), was given a responsibility of performing this review. In UTSI's efforts to review the available options, Oak Ridge National Laboratory, (ORNL), especially Mr. Robert Hawsey and Dr. M. Paranthaman provided very valuable guidance and technical assistance.

This report describes the review carried out by the UTSI staff, students and faculty members. In particular, the report includes:

- Process Flow Schemes and Involved Operations
- Multi-Attribute Analysis Carried out for Objective and Subjective Criteria
- Manufacturing Parameters to Process 6,000 km/year of Quality Coated Conductor Material

- Metal Organics Decomposition (MOD), Sol-Gel, MOCVD, E-beam and PLD as the Leading Candidates, and Technical Concerns/Issues that Need to be Resolved to Develop a Commercially Viable Option Out of Each of Them.

This report also includes generic areas in which additional research and development work are needed. In general, it is our feeling that the science and chemistry that are being developed in the coated conductor wire program now need proper engineering assistance/viewpoints to develop leading options into a viable commercial process.

2.0 Introduction

The purpose of the present study is to assess various manufacturing processes and their potential applicability to manufacturing of coated high temperature superconductors. There presently is no infrastructure for making long length coated conductors. The capability to make long length particulate based high temperature superconductors, which are primarily made by drawing operation, are similar to the methods of producing conventional non-superconducting wire. On the other hand, coated conductors have only been produced in a laboratory environment and have a characteristic area of a few square centimeters. The coated conductors potentially have more superior performance than available drawn conductors in that they can have higher critical field and temperatures. The increased performance is due to the differences in materials rather than the processes and the drawing operations cannot be used with materials employed in coated conductors. In the present study of coated conductor manufacturing, only YBCO is considered in recognition of its extensive study to date. The objective in studying and characterizing the various potential manufacturing processes is to identify the processes which have the highest potential to be developed for the commercial application.

In the case of production of a coated conductor in long lengths, there are two figures of merit: current capacity and cost. Any conductor will have to meet some minimal value of engineering current density where the minimum value is application specific. That is to say that it will in general always be desirable to maximize the engineering current density, but the minimum acceptable values will be different in the cases of a motor field winding and underground transmission cables.

The YBCO material has a characteristic critical current of the order of 1.0×10^6 amps/cm² when observed on single crystals of the parent material. In a multi-crystalline structure, the critical current density is drastically reduced by the presence of crystalline boundaries and is termed the "weak link" behavior. In thin films, it is desired to grow the films maintaining a high order or texture in the film such that a highly aligned crystalline matrix having low angle grain boundaries results. When this is successfully accomplished the film intra granular critical current density approaches the film intra granular current density. As will be more fully discussed later, the HTSC films are thin and only of the order of a few microns thick. Consequently, the films are deposited on a metallic strip for strength. It is believed that, while handling problems are obvious, the metal strip can be as thin as 1 mil (25 microns). YBCO is subject to degradation by moisture so any thin film would require a hermetic seal as well as obvious electrical insulation. The engineering current density is the critical current ratioed to the superconductor cross section, divided by the total conductor cross sectional area. It is easy to see that when the cross sectional overhead due to the metallic substrate and environmental encapsulation is taken into account, the engineering current density is only a fraction of the superconducting material critical current density. From the outset it is therefore desirable to maximize both the HTSC critical current density of the superconducting film and the superconductor cross sectional area relative to the total conductor cross sectional area.

Two methods of maximizing the superconducting materials cross sectional area are obvious: Increasing the film thickness and coating both sides of the metallic substrate. The latter is a complication of the manufacturing process and may not be practical in all cases, as for example if the substrate requires heating to insure proper film growth. The former process is not straight forward either as there is evidence that the film critical current density maximizes for thicknesses of a few microns. For submicron thicknesses, or for the first fractional micron thicknesses of thick films, the critical current density is lowered due to misalignment of the crystalline ab-planes and for thick films the c-axis alignment normal to the substrate plane deteriorates. In all cases biaxial alignment, in the ab-plane and c-axis direction, is a prerequisite for high intergranular critical current density.

The second element for assessing a candidate manufacturing process is cost. This element has many facets. Processes requiring high vacuums will be more costly than an atmospheric pressure process, processes having many sequential operations correspondingly have increased costs, materials costs, processing speeds, and environmental contaminants all combine to determine the final cost. In this study, costs per se are not determined, but rather the processes are defined and characterized in sufficient detail that one could conceivably estimate the cost for a process. The process parameters and controls and material processing rates for the processes considered are all given as estimates. All data presented are taken from the open literature. In many cases, the methods employed in the laboratory scale environment

may themselves not be scalable to a commercial scale without incurring developmental studies and costs which are not considered herein.

2.1 Potential Scale-Up Issues

In scaling up the data developed from various laboratory scale work to a large scale, continuous mode processing plant, several issues come up. However, the major issues that need to be addressed for a successful scale-up are as follows:

Related to Superconducting Film Thickness

The manufacturing of coated conductors requires that high quality films be deposited on substrates at high rates. The superconducting layer will be relatively "thick," in the range of 1 to 10 micrometers, whereas buffer layers, diffusion barriers, passivation layers, etc. can be thinner. Since the thinnest commercial metal tape substrates (e.g., of oxidation-resistant nickel superalloys) are about 1 mil (25 micrometers) in thickness, it is important to have a thick superconducting film, so that the high J_c (critical current density) translates to high J_e (engineering current density). The maximum permissible thickness of the superconducting layer is not yet known. Thicker layers are stiffer and more prone to fracture; they are also more prone to delamination due to differential thermal expansion during processing. However, it is clear from a number of studies that films several micrometers in thickness will be acceptable. A plausible cross section of a future coated conductor is a 20 micrometer metal tape, coated on both sides with a buffer layer, a 5 micrometer YBCO layer, and capped with a 0.5 micrometer passivation layer.

For YBCO of thickness higher than 5 micrometers, there are intrinsic obstacles since

- 1) a-axis grains start forming
- 2) there is insufficient oxygenation as thickness increases
- 3) defects accumulate and degrade J_c

However, some workers⁽¹⁾ have stated that they saw no rapid fall-off of J_c in thicker films. A recent paper by Freyhardt's group at Gottingen shows how inadequate temperature control (substrate temperature falling due to increasing infrared emittance during processing) can result in a-axis grains nucleating in the YBCO films at thicknesses near 2 micrometers. By improving their depositions, they obtained fully c-axis films as thick as 5 micrometers⁽²⁾.

Although the goal that a future conductor may have a 20-micrometer metal substrate with 5-micrometer YBCO films on both sides, is aggressive, the desire for high technical and economic performance will eventually result in conductors with a high percentage of high- J_c superconductor in the cross section. It is known that YBCO can withstand up to 0.5% strain in tension (more in compression). A recent paper from LANL (Los Alamos National Laboratory), demonstrates that compressive strains of 1% and tensile strains of 0.4% are permissible⁽³⁾. For a 30-micrometer structure, 0.5% strain corresponds to a bending radius of $(1/2)(0.03 \text{ mm})(1/0.005) = 3 \text{ mm}$, which is acceptable for most applications. Also, the LANL work, and earlier work in Japan as well show rather directly that the films on metal substrates can be bent. Future thinner metal substrates will just result in increased flexibility.

Recent developments in increasing the area of deposition are also worthy of mention. The session on coated conductors at the 1997 Applied Superconductivity Conference showed that the German/Siemens effort has really matured; they are now helping shape the state of the art. F. Freyhardt of Gottingen specializes with large area deposition of YBCO (up to 20 by 20 cm), by e-beam evaporation. The substrates rotate during deposition so that they are alternately exposed to a flux of metal atoms in a fairly high vacuum, followed by passage through a chamber with higher oxygen pressure. While Freyhardt also does IBAD (ion-beam assisted deposition), it appears that his colleague H. Kinder in Munich, is now taking the lead in this area. Thus Kinder does IBAD deposition of YSZ on metal and other substrates, capping the structure with a thin Y_2O_3 layer, and then sends samples to Freyhardt for the YBCO deposition. They also showed a picture of their structure made for a current limiter at this '97 conference. It was a 20 by 20 cm substrate (possibly poly-YSZ; it could have been metal), with a YBCO coating. Siemens had patterned the conductor into a serpentine pattern of width, about 1 cm. At this '97 conference, Freyhardt commented that they have the capability to make about 10 km/yr of tape conductor (if they wanted to) at present.

Related to Film Deposition Rates

Most YBCO films fabricated to date have been deposited over centimeter-sized substrates during a period of a few minutes to hours. In these laboratory studies the primary concern is film quality, not deposition speed. Straightforward scale up entails deposition on larger substrates, and increasing the power to the deposition apparatus to boost rates until film quality begins to degrade. There is no question that long lengths of high-performance conductor can be synthesized by these straightforward methods. The key question at the present time is whether these long lengths be manufactured economically. If the value of a tape 1 cm wide is *roughly* \$ 1/meter, then a small manufacturing plant with a value of tens of millions of dollars, must produce several million meters of tape per year, to justify the investment. This areal rate of production translates to a minimum hourly rate of a few square meters per hour, in contrast with current laboratory rates of a few square centimeters per hour. Thus **film deposition rates must increase by about 4 orders of magnitude**. While the projected areal rate is high, the volume of superconductor to be deposited per hour will only be a few tens of cubic centimeters per hour.

Much of the needed gain in deposition speed can be obtained by scaling up the size of the deposition zone from a few square centimeter to a few square meters. However, it is clearly advantageous and preferable to improve the specific film deposition rate (that is, rate of film thickness increase in dimensions of micrometers per minute), which would permit the use of a smaller deposition zone.

Small-scale laboratory deposition rates are typically only a few angstroms per second; the growth of a micrometer thick film then requires roughly an hour. Since one would like to deposit at least a few square meters per hour, the size of the deposition equipment would need to be rather large. An order of magnitude increase in deposition rate can permit the deposition chamber dimension to be reduced by a factor of 3, and the cost of the chamber correspondingly can probably fall by a factor of about 30. Thus, there is a significant incentive to increase deposition rates. For very thin buffer layers, the deposition rate may be less critical.

Each film deposition process will have some maximum rate, beyond which defects or other problems such as supplying source material or removing by-products may become limiting. For example, diffusion of the depositing atoms on the growing film surface requires time. If the deposition rate is too high, then some atoms will not have time to diffuse to their "proper" sites. Research is ongoing to determine what these maximum rates are for various processes.

A few specific examples from the published literature can indicate some of the increased rates achieved so far. For pulsed laser deposition, YBCO coatings have been formed at rates higher than 1 micrometer per minute. This is done by increasing the pulse rate of the laser. Unfortunately, the size of the laser plume is such that only a small number of square centimeters of substrate can be coated by a single laser, so that larger lasers and multiple lasers would appear to be required. With photo-assisted MOCVD, rates on the order of 1 micrometer per minute of YBCO have also been achieved⁽⁴⁾. In this case, the present high cost of the precursor metal organics compounds is an issue.

E-beam co-evaporation is believed to have considerable potential for large area deposition at high rates. One recent paper⁽⁵⁾ reports a technique for coating substrates up to 9 inches in diameter with YBCO, at nominal rates of 24 nm/min. For co-evaporation, an important issue can be the accurate balance of evaporation rates from the separate Y, Ba, and Cu sources.

For relatively thick YBCO films, grown at high speed, it can be expected that oxygen annealing will require attention. In small scale growth, the films are generally cooled slowly from a high deposition temperature (above 700°C) in oxygen. During this cooling oxygen is absorbed by the films (at 400 to 500°C), and the non-superconducting tetragonal phase is converted to the superconducting orthorhombic phase. Since this oxygen diffusion is a relatively slow process, particularly in the c-axis direction, it is anticipated that spools of YBCO tape may need to be batch annealed to ensure adequate oxygen uptake.

3.0 Description of Typical HTSC Wire/Tape Manufacturing System

To evaluate various processing options for depositing epitaxial buffer and superconductor layers, one needs to describe the general scheme as well as prior knowledge in the other HTS processing systems and their limitations.

The development of high- T_c superconducting thin films on metallic substrates is of great importance from the point of view of their applications in preparing superconducting magnets, cables, electromagnetic shields, etc. In the last few years, a major worldwide research effort has been devoted to the Oxide-Powder-In-Tube (OPIT) method to make high- T_c superconducting wires and tapes. However, this OPIT process can only be applied to Bi- or Tl- based oxide superconductors. It seems that by sequential and repetitive operations of mechanical rolling and drawing other systems are not able to provide acceptable superconductor quality. Taking advantage of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO), which has its irreversibility line at higher temperatures even with a lower superconducting transition temperature as compared to Bi- and Tl based conductors, applications at 77K and in magnetic fields over 1T will be possible. However, the OPIT technique when applied to YBCO systems does not provide acceptable products. Hence, researchers trying to develop YBCO based superconductors have been attempting a number of physical and non-physical (chemical) deposition methods.

In some of the earlier thin-film deposition research, a post-annealing step at temperature $\geq 900^\circ\text{C}$ was required after a deposition at a lower temperature. This caused a considerable interface reaction between the substrate and the film; and resulted in various undesirable epitaxial orientations. It is commonly believed that a good orientation of films, a minimization of grain boundaries, and the prevention of interdiffusion are some of the important parameters to achieve high critical current density (J_c). Most of the reported experimental research focused on HTS film growth on single-crystal dielectric substrates, using physical deposition techniques such as laser ablation, sputtering, evaporation, and thermal/plasma-enhanced chemical vapor deposition. However, resulting products were not suitable for applications as in coils, magnets and power transmission lines. As a result, a significant portion of the experimental efforts was redirected to grow HTS films on metallic substrates.

Conceptually, the manufacture of HTS thin film conductors or tapes will consist of a means of epitaxially growing the HTS on a suitable starting substrate. The substrate must provide a suitably textured surface to promote the required ordered growth of the HTS crystals such that low angle grain boundaries result. This in turn implies that the surface lattice dimensions should be compatible with those of the HTSC. In addition, the substrate should possess the strength and flexibility required of a conductor and have a favorable match of its thermal expansion with that of the superconductor. The substrate material should also be thermally and chemically compatible with any of the intermediate deposition or growth processes involved in creating the superconducting film on its surface.

While single crystals can be used as starting substrates for certain electronic applications of HTS thin films, no single crystal material substrate for conductor applications has been found. Current research indicates that the substrate of choice will be a composite comprised of a thin metal strip with one or more overlying buffer layers. The metal strip provides the basic strength and flexibility to the composite structure. The buffer layers, which are thin film depositions, provide for chemical isolation of the metal strip as well as the necessary final surface texture for the HTS material to be epitaxially grown upon. The composite substrate must also be inert to any thermal or chemical reactions incurred during the steps in the deposition or growth of the HTS film and thus a single composite substrate may not be applicable for all deposition processes. Finally, in addition to the crystal lattice matching criteria between the substrate and the HTS film, the thermal expansion characteristics between the substrate and the HTS film should be closely matched to preclude cracking or delamination.

Two processes for producing metallic substrates are currently being extensively studied. The processes differ in general in the method in which the surface texture is created. In the first process, termed the Rolling Assisted Biaxially Textured Substrate (RABiTS) process, the starting metal strip is hot rolled and annealed to promote a textured surface on the metal strip as depicted in Figure 1. Many metals are amenable to mechanical texturing in this fashion but the present metal of choice is high purity nickel. As shown in the figure, after the metal is mechanically textured a buffer layer is applied. In Figure 1 the buffer

layer is applied using a pulsed laser deposition but could equally be based on a sputtering process or electron beam evaporation process. The process depicted is suitable for buffer materials which can be vaporized and recondensed on the substrate surface in an oxygen depleted environment at an elevated temperature. Departure from these conditions could result in oxidation of the nickel surface defeating the replication of the texture or ultimately resulting in the diffusion of nickel into the HTS film. In a particular application, ORNL uses pulsed laser deposition of yttria stabilized zirconia, YSZ, as the initial buffer layer on a textured a high purity nickel base. It is found that the YSZ replicates and enhances the metal texture. That is to say that the resulting YSZ surface texture is improved over that of the underlying metal surface. ORNL has also found that further improvement can be realized when a second layer of cerium oxide film is deposited over the YSZ. Note that in this case, the process could not be done in reverse order, i.e., the CeO_2 being placed first, by reason of the propensity for nickel to easily oxidize using oxygen from CeO_2 .

In Figure 2, a variant of the RABiTS process is depicted wherein a lanthanum aluminate buffer layer is grown on a textured metal strip by a repetitive sol-gel process. The repetitive steps of dip coating and pyrolyzing are required to attain the desired film thickness. The point is that one can have a variety of buffer materials and processes for applying them, but if the concept of building on the starting metal texture is used, it is termed a RABiTS process in the present study. The potential advantage of the RABiTS process is the throughput speed which is limited in principle by the buffer application steps.

The second process for making metallic textured substrates is the Ion Beam Assisted Deposition (IBAD) process depicted in Figure 3. This process differs from the previous RABiTS process in that no texture is forced on the starting metal strip but rather the first buffer layer laid on the metal strip is forced to have a preferred texture independent of the underlying metal strip. This is accomplished by using an ion beam impinging on the thin film buffer surface as it is being laid down in a vapor phase deposition. The impinging ions from the ion beam selectively cause re-emission of particles from the growing surface which have a certain alignment. This is equivalent to leaving particles which have a particular desirable alignment and that is the basis of the process. Thus in the IBAD process, the required surface texture results from the initial buffer layer deposition rather than using the metal surface as an initial growth template. Various metals could potentially be used as the substrate base metal but at LANL where the process has been most promoted, Hastelloy, a high nickel alloy is the preferred choice. Hastelloy has a good thermal expansion match with the buffer material used as well as the HTS films, notably YBCO. The IBAD process is an extremely slow process and by its general nature is carried out only in combination with a vapor phase deposition process. An ion beam is shown in Figure 3 as the source for vaporizing the buffer material (YSZ) but a laser powered or a sputtering scheme could be equally considered. Like the RABiTS process, the IBAD process is a family of possible processes which involve various buffer and base metal materials. The distinguishing characteristic of the IBAD process is that an ion beam is used to promote texture in the initial buffer layer regardless of the multitude of possible processes for application of subsequent buffer layers.

The published literature on various schemes to form HTS films on metallic, semi-metallic or ceramic substrates can be divided into:

- physical methods, and
- non-physical or chemical methods

Under physical methods, the following deposition schemes have been evaluated⁽⁶⁾:

- Sputter Deposition
 - + Magnetron Sputter Deposition (both RF and DC mode)
 - + Ion-beam Sputter Deposition (both RF and DC mode)

IL-1957b

Figure 1. Textured Substrate Preparation Method Following “RABITS” Scheme and Pulsed Laser-Based Buffer Deposition

IL-1903a

Figure 2. Texturized Substrate Preparation Method Following "RABITS" Scheme and Sol-Gel Based Buffer Deposition

Figure 3. Texturized Substrate Preparation Method Following "IBAD" Scheme

- Electron Beam Evaporation
 - + Co-Evaporation (Using Resistive Heating also)
 - + Activated (Plasma)Reactive Evaporation (Includes Resistive Heating and Ion-Beam Assisted)
- Flash Evaporation
- Plasma Spray
- Molecular Beam Epitaxy (MBE), and
- Laser Ablation (includes Ion-Beam Assisted)

In addition, the following two methods which are based on depositing the powdered deposits (either in slurry or suspension forms) have also been evaluated.⁽⁶⁾

- From Powder Suspensions or Slurries by Spin-Casting/Dip-Coating/Screen-Painting, etc.
- Electrophoresis

Among the non-physical or chemical or solution-growth techniques, the following methods have been studied:⁽⁶⁾

- Chemical Vapor Deposition (CVD) Techniques
 - + Metal Organics Chemical Vapor Deposition (MOCVD)
 - + Plasma or Photo-Assisted MOCVD
- Sol-Gel (Spin/Dip-Coating, Spraying, Painting)
- Metal Organics Decomposition (MOD) [Includes Spin/Dip Coating, Spraying, Painting, etc.]
- Electrodeposition, and
- Aerosol/Spray Pyrolysis

Besides the technique involved in depositing the material, and transmitting the energy necessary for vaporization and deposition, the major differences in the physical and chemical techniques relate to:

- what is the starting material (precursor or YBCO itself)
- any thermal decomposition, oxidation or other chemical reactions taking place
- does the deposited material need post-annealing for physical as well as chemical transformation

In addition, the chemical methods usually need lower energy level and less severe process conditions. For each individual concept, all these differences are discussed later on.

Except the electrophoresis technique evaluated by the scientists at the General Atomics⁽⁷⁾, none of the published work started with a metal substrate on one end and end up with the coated material at the other end. In order to develop appropriate conductor coating schemes for the continuous processing/manufacturing of long wires or tapes or ribbons, additional steps that were not tested originally need to be included. In general, a spool-to-spool or reel-to-reel type of continuous manufacturing scheme developed out of any of the above techniques, would consist of at least the following operations:

- preparation of metal tape substrate material
- preparation and application of the buffer layer(s)
- preparation and application of the HTS material and required post-annealing, and
- preparation and application of the external passivation/insulation layer

As it can be seen these four major operations are necessary because of the complete match required between the four major components of the finished HTSC wires/tapes. The four major components are thus, metal substrate, buffer, HTS and outer passivation/insulation layer. From our literature search no information was found about any work that has taken the concept from the metal substrate at one end and produced a finished insulated wire product at the other end. Most of the work described either working with single crystals of buffer material and/or small samples of metal substrate. For evaluating the candidate options for the continuous processing/manufacturing of long length of coated wires, it was therefore necessary to conceptually develop schemes that would incorporate the above operating steps and enable one to produce long lengths of wire in a reel-to-reel or spool-to-spool mode. Based on the available literature, and from talking to the various experts in the fields, we were able to put together the process schematics for the following options:

- Sol-Gel
- Chemical Vapor Deposition (CVD)
- Metal Organics Chemical Vapor Deposition (MOCVD)
- Metal Organics Decomposition (MOD)
- Electrodeposition
- Electrophoresis
- Aerosol/Spray Pyrolysis
- Pulsed Laser Ablation/Deposition (PLA/PLD)
- Electron Beam-Based Deposition

Recently, Liquid Phase Epitaxial (LPE) growth method requiring a seed layer of YBCO over a suitably textured substrate is being developed in Japan and Germany. Required seed layer of YBCO for this method can be developed using any of the physical vapor deposition methods listed above. From a molten salt bath of YBCO and suitable flux material, a thick layer of YBCO is applied to the seed-coated substrate by dip-coating. Since this method is still being developed, at present, enough information is not available to include it in this evaluation. In the future, if this and the other such emerging methods are found feasible for the manufacturing of the long-length coated conductors then they should certainly be included in the revised evaluations. Meanwhile, for the current evaluation only the nine options listed above are included in this work. The process schematics for each of these nine candidate options are shown in Figures 4-12. In each of these schemes, we have shown only the HTS deposition step and required subsequent annealing. The preceding steps corresponding to metal tape substrate preparation and metallic substrate preparation can follow any of the schemes shown earlier in Figures 1 - 3. Thus, one can have metallic substrate prepared by either RABiTS scheme or IBAD scheme over which the HTS film can be deposited using any one of the nine schemes shown in Figures 4-12. The brief descriptions on each of these nine flow sheets for depositing HTS film are as follows:

Figure 4. Conductor Coating Scheme Following PLD Method

3.1 Pulse Laser Deposition/Ablation

Process schematic incorporating pulse laser-based YBCO deposition is shown in Figure 4. The major operating steps involved in this scheme are:

- YBCO is prepared separately by mixing the raw ingredients (Y_2O_3 , BaCO_3 and CuO) in the necessary proportions then calcining the mixture and pulverizing the product to the necessary particle size. One can also buy the ready made YBCO powder if available at an acceptable price
- Ground YBCO powder is then used in forming the YBCO film over the textured substrate tape (e.g. $\text{CeO}_2/\text{YSZ}/\text{Ni}$ -rich tape) of required thickness. For YBCO deposition, it is assumed that the temperature would be around 800°C , and laser-based technique would be employed at low pressure in low O_2/N_2 -containing atmosphere.
- Off-gases from this YBCO chamber are led to the recovery/disposal section.
- The YBCO-deposited tape would usually then go through a stage (which is not shown here as it is not yet decided) where some kind of passivation/insulation layer would be formed before winding the finished tape on the spool.

According to recent information from the Oak Ridge National Laboratory (ORNL)⁽⁸⁾, on the RABiTS-based textured substrate, the application of two layers of buffer material is not now necessary. Using sputtering and/or electron beam deposition technique instead of pulsed- laser ablation, as shown here, the scientists at ORNL have grown a YBCO film on a 0.5 micron thick layer of CeO_2 without using the initial layer of YSZ. The resulting material has given a J_c value of about $1 \times 10^6 \text{ A/cm}^2$ at 75K. If this ORNL result is consistently confirmed in the future then the scheme based on PLD type deposition can be simplified further by eliminating one layer of buffer material.

3.2 E-Beam Based Deposition

Process schematic incorporating YBCO deposition by E-beam technique is shown in Figure 5⁽⁹⁾. The major steps involved in this E-Beam based deposition of YBCO on suitable textured substrate are as follows:

- In a closed chamber, elemental Y, Ba (from BaF_2) and Cu are vaporized from their respective containers and then deposited in an oxide form corresponding to YBCO stoichiometry over a suitably textured substrate tape. Oxygen necessary for oxide formation is provided in an atomic form by the atomic oxygen generator. The pressure in the chamber is maintained at a very low level, and the substrate temperature is maintained around 740°C .
- Off-gases from this chamber will contain fluorine compounds, and therefore will be led to appropriate recovery, treatment or disposal step.
- Again the type of final passivation/insulation layer or technique to apply it are not yet available, and therefore, this particular step is not shown here.
- The finished product will be then wound on a spool.

3.3 Metal Organics Chemical Vapor Deposition (MOCVD)

In the previous two schemes, YBCO was either prepared a priori and then deposited on the textured substrate (as in PLD scheme) or was produced in-situ by depositing elements and immediate oxidation (as in E-beam scheme). But in both the cases, the resulting coated material did not need further annealing at high temperature to complete the oxidation and crystallization of the deposited film in an epitaxial manner. The schemes that are presented now usually use some kind of precursor to introduce Y, Ba and Cu species on the substrate and then need some kind of chemical decomposition reaction to eliminate the carrier. The resulting film is not in a proper oxide form, and therefore, further oxidation of the film as well as crystallization of the

resulting material is necessary to get epitaxially formed YBCO-coated conductor tape. Thus the major difference between the physical methods of deposition (e.g. PLD and E-beam) from non-physical or chemical deposition methods is in the areas of how the chemical forms of the Y, Ba, Cu species are brought into the deposition chamber and in need for the subsequent oxidation/annealing/cooling steps.

Figure 5.E-Beam Based Conductor Coating Method

One such chemical deposition method is called MOCVD-metal organics chemical vapor deposition. In this scheme, the Y, Ba and Cu precursors are introduced in a highly pure metal organics form by vaporizing and introducing the vapors in the MOCVD chamber. Process schematic to produce YBCO-coated conductor tape following the MOCVD technique is shown in Figure 6. Again, all the steps are not shown here and even

Figure 6. Conductor Coating Scheme Following MOCVD Method

the ones shown here need not be carried out at one site from end to end. The major operating steps visualized in this scheme are as follows:

- Preparation of metal organics ---precursor solution

This step usually would be carried out off-site by some chemicals manufacturing company and the conductor coating company would probably buy the solution mixture from them. It is anticipated that a mixture of Y(THMD)₃, Ba(THMD)₂ and Cu(THMD)₂ (where THMD stands for 2,2,6,6-tetra methyl -3-5 Heptanedionate or generically called as β -diketonate) would be prepared in an organic solvent mix that consists of tetrahydrofuran (THF), isopropanol and tetraglyme. The details about synthesizing individual precursor or mixing are not available at present in the literature. But, it is believed to be very sensitive to levels of contaminants and as a result the cost of such metal organics are believed to be very high in the range of \$100- \$300 per 10 gram sample.

- Textured substrate tape (e.g. YSZ/CeO₂/Ni-rich) enters the MOCVD chamber. The tape is maintained in this chamber at 600-850°C and the chamber pressure is kept at about 1-10mm Hg. The N₂O/O₂ plasma is introduced from the plasma generator tube and vapors of Y, - Ba, - Cu, - precursors are brought in by flowing N₂ at about 230°C. No one has carried out such MOCVD application on wire/tape in a continuous fashion and from both sides. Hence at this stage it is more of a conceptual design that assumes a number of passes for the tape between the rollers to achieve desired thickness of the HTS coating at the desired deposition rate.

- Off-gases from the MOCVD chamber will contain mostly organics that come off the precursor solution and would need to be appropriately handled in the recovery/disposal section.

- Since subsequent oxidation/annealing/cooling need longer time and involve a number of heating/cooling steps, material coming out of the MOCVD chamber will need to be wound on a spool and number of such spools or each individual spool can go through the necessary heat treatment to develop textured crystalline structure of the resulting HTS film.

- In the oxidation/annealing and cooling chambers the partial pressure of O₂ will be kept low and the temperature progression would follow the ones recommended from the laboratory scale work.

- Off-gases from these heat treatment steps will be led to the section where recovery or disposal-related operations would be carried out.

- Again the final passivation/insulation layer or the technique to apply it are not identified yet. Hence, that particular step is not shown in this schematic, but in a commercial process such a step will be required. In the end the finished product will be available on a spool.

3.4 Sol-Gel Method

This option is based on the solution growth technique and does not use any high energy particles (ions, electrons, photons, etc.) for transportation and vaporization of the coating material for subsequent coating on the substrate. In that respect it is thus considered to be utilizing a conventional technology of coating a liquid film and drying it. A process schematic which incorporates forming a superconductor layer (e.g. YBCO) by this sol-gel technique over a suitably textured substrate tape is shown in Figure 7. The major steps involved in the proposed scheme are as follows:

- Preparation of gel/solution containing precursor for YBCO.

Figure 7. Conductor Coating Scheme Following Sol-Gel Method

- The YBCO precursor solution will most likely be prepared off-site and available in a container from which it will be pumped for distribution to different coating chambers. However, based on the literature information⁽¹⁰⁾, it is believed that the supplier of such a gel/solution would need the following steps to prepare it.
- Organic solutions of Ba-alkoxide and Y-alkoxide in 2-methoxy ethanol are mixed with the solution of copper oxide in pyridine. The mixture then undergoes vacuum distillation in the presence of additional 2-methoxy ethanol. The resulting solution is then partially hydrolyzed to produce a gel/solution of YBCO precursor of required concentration and flow characteristics. Also, the alcohol vapors coming out of the distillation step would need some kind of recovery/disposal operation.
- The suitably textured substrate tape is coated with the YBCO precursor gel/solution. It is believed that a number of such coating chambers would be needed to produce films of uniform crystalline structure and overall thickness.
- In between each coating chamber the deposited material will be pyrolyzed under oxygen atmosphere at 150-250°C to vaporize organic solvent and to oxidize. By doing so in small steps, it is believed that some crystallization also takes place during this operation with the already deposited/textured earlier layers.
- Although not shown here, but each coating chamber will need some kind of a recirculation system for precursor gel/solution to maintain the required concentration of precursor, to bleed portions of the undesirable contaminants acquired from coating and to maintain the flow and coating characteristics of the circulating gel/solution. The material that is taken out in a slip/bleed stream will need some kind of recovery/disposal operation.
- Similarly, off-gases coming out from each pyrolyzer would need some kind of recovery/disposal operation in addition to appropriate waste heat recovery system.
- The HTS-coated tape is now wound on a spool for further heat treatment in a batch mode. It is possible that the required heat treatment is given to a number of such spools at the same time or one spool at a time. The first stage of this thermal treatment involves complete oxidation at 795°C to the YBCO phase followed by progressive cooling in an oxidizing atmosphere to room temperature.
- Before sending out to the customer, the HTS-coated tape will be coated with an appropriate passivation/insulation layer. But, it is not yet decided what that layer will be and how it will be applied.

3.5 Chemical Vapor Deposition (CVD)

This particular chemical coating option uses commonly available precursor salts for the ingredients of YBCO and as a result such salts are expected to be cheaper than the metal organics precursors used in the other options. The scheme employing chemical vapor deposition on a suitably textured substrate tape is shown in Figure 8. The major operations involved in this scheme would be as follows:

- Preparation of precursor salts vapor mix

A vapor mixture consisting of stoichiometric amounts of Y (from YCl_3), Ba (from BaI_2), and Cu (from CuCl) is prepared by vaporizing each halide at high temperature and then carrying the generated vapors with nitrogen to a common mixing point. Based on the literature⁽¹¹⁾ temperatures for vaporization are maintained at 820°C for YCl_3 , 950°C for BaI_2 and 340°C for CuCl .

- The suitably textured substrate tape is introduced through a number of chambers if necessary, to achieve overall thickness of the YBCO film. Each chamber would have the tape making multiple passes and being uniformly coated by the vapor mix of YBCO precursors brought in by the nitrogen carrier gas. In each chamber moist O_2 will also be introduced and the chamber temperature of 750-950°C and pressure of 20mm Hg would be maintained. In commercial practice, it is possible that one big chamber with tape making a large number of passes is preferred rather than a number of small chambers where tape would make only a few passes.
- Off-gases from each chamber will contain halogens (Cl_2 , I_2) as well as respective acids such as HCl, and HI. Such a mix would be very corrosive and would need appropriate treatment (absorption, neutralization, etc.) before disposal in an environmentally acceptable manner.
- The tape coming out of the last vapor deposition chamber is then wound on a spool so that further thermal treatment involving oxidizing and cooling can be conveniently carried out in a batch or semi-batch mode. By doing so, a number of such spools can be attached to some kind of a slow-moving assembly line type arrangement. This thermal treatment will be carried out under necessary O_2 atmosphere to ensure complete oxidation to YBCO phase and conversion to required epitaxial crystalline form. Off-gases coming from such chambers would still contain some halogen-containing species and therefore, would need to be appropriately treated prior to disposal.
- The YBCO-coated tape then would be coated with some kind of passivation/insulation layer, but its type as well as method of application are not yet determined. As a result, this is not shown in Figure 8.

3.6 Aerosol/Spray Pyrolysis

This is another chemical coating technique that uses precursor salts in commercially easily available forms and as a result should be significantly cheaper than the metal organics precursor salts. Again, in the literature no attempts have been mentioned starting with the metal tape at one end and ending up with the coated conductor at the other end. As a result, we have assumed that a suitably textured substrate tape should work fine for spray coating the nitrate solution. With this assumption a process scheme for YBCO precursor coating system based on aerosol spray/pyrolysis is prepared and shown in Figure 9. The major operations involved in this scheme are as follows:

- Preparation of precursor salts solution

An aqueous solution containing $Y(NO_3)_3$, $Ba(NO_3)_2$ and $Cu(NO_3)_2$ in stoichiometric amounts is prepared from high-purity commercially available nitrates and deionized double or triple distilled water^(12,13). This aqueous solution of nitrates is then atomized in various spray chambers to provide the coating of nitrate precursor on a suitable substrate.

- The suitably textured substrate tape is introduced into a spray chamber where aqueous solution of nitrates is sprayed in a finely atomized/aerosol form from both sides of the tape. The tape speed, the chamber temperature and O_2 partial pressure in the chamber are maintained such that solution film will not drain off the tape. It is believed that to get desired overall thickness and the uniformity of deposited film, more than one such spray chamber may be needed.
- From spray chamber the tape would go to a preheater maintained at about 600-800°C in the air atmosphere. Here nitrate precursors would decompose and form oxide layers.
- This spraying of nitrate aerosol and preheating/decomposition is continued in a number of stages in a series till overall thickness of the YBCO layer as well as the epitaxial texture of the composite are achieved.

Figure 8. Conductor Coating Scheme Following CVD Method

Figure 9. Conductor Coating Scheme Following Aerosol/Spray Pyrolysis Method

- Off-gases from the spray chambers as well as preheaters will contain mostly nitrogen species and unutilized precursor salts. This would need some kind of recovery and treatment step prior to disposal. Similarly, each spray chamber will need some kind of liquid recirculation system to capture excess liquid collected at the bottom of the chamber. A slip stream may be then taken out of this recirculation loop to control the buildup of impurities.
- From the final preheater the coated tape would be wound on a spool and the spool by itself or in a group with the other similar spools will undergo appropriate thermal treatment.
- In the first phase of thermal treatment, the spools will be kept at 800-950°C under proper O₂ partial pressure to ensure complete oxidation and crystallization to required texture.
- In the next phase, the heated spools will be cooled to 500°C and then to room temperature at accepted rates under oxygen atmosphere.
- Off-gases from the thermal treatment components will be led to the section where some type of recovery or treatment operations will be needed prior to disposal.
- The material coming out of the cooler will usually undergo some kind of coating with a passivation/insulation layer. But details about this protective layer or its method of application are not available at present.

3.7 Metal Organics Decomposition (MOD) Method

This method is very similar to the aerosol/spray pyrolysis method described above. The major differences are in the areas of:

- Use of trifluoroacetates of Y, Ba and Cu as a precursor in an organic solvent versus aqueous solution of nitrates, and
- Use of the dip coating technique rather than the aerosol spray technique.

Because of the above differences, the temperatures employed in the dip coater and pyrolyzer (or oven as identified here) are significantly lower. Again due to limited information available in the literature on this concept, we have assumed that dip coating of trifluoroacetate precursor solution can be carried out on any suitably textured substrate tape. The process scheme employing metal organics decomposition (MOD) option is shown in Figure 10. The major operations involved in this scheme are as follows:

- Preparation of precursor salts solution.

Commercially available acetates of Ba, Y and copper are dissolved in stoichiometric quantities in water and then mixed with trifluoroacetic acid to form trifluoroacetates of Ba, Y and Cu. The resulting mixture is then dried and the dried material is then redissolved in methanol solvent to provide an organic solution of precursor salts⁽¹⁴⁾. It is possible that for commercial application, this particular step may be carried at the chemical supplier's place. In that case the organic precursor solution will be available in large containers from which it will be supplied to various dip-coating tanks.

- The suitably textured substrate tape is introduced into a dip-coating tank where precursor salts solution is filled to the desired level. The tape speed is maintained so as to get desired film thickness in one stage. Liquid content of the tank will be in a continuous recirculation mode to maintain desired strength of the precursors in the solution. A slip stream may be needed from this recirculation loop to control the buildup of the impurities at the desired/acceptable level. This slip stream will need appropriate recovery or treatment step prior to recycle or disposal.

Figure 10. Conductor Coating Scheme Following MOD Method

- The coated tape then enters the oven maintained at about 200-400°C under O₂ atmosphere. At these conditions water of crystallization and excess of solvent are removed; and the trifluoroacetate film decomposes to the oxyfluoride form. If the desired thickness of the film is not achieved in one such coating/baking sequence then several such sequences are carried out in a series type of operations to achieve the desired overall thickness. In a commercial practice, it may be possible to use only one very large dip coating tank and appropriate tape speed to achieve the desired overall film thickness.
- Off-gases from each of the baking ovens would be led to the section where some kind of recovery or treatment operations would be needed.
- Tape coming out of the final oven will be wound on a spool for subsequent thermal treatment in a batch or semi-batch mode. Either a number of such spools will be heat treated simultaneously or each one will undergo such treatment in an assembly line type of a setup.
- In the first stage of thermal treatment, the spools containing coated tapes undergo further decomposition in a moist N₂/O₂ atmosphere where oxyfluoride form of the precursor gets converted to the desired YBCO phase and the crystallization is also completed.
- In the second stage the tape undergoes cooling at a controlled rate in the O₂ atmosphere.
- Off-gases from both these stages will need some kind of recovery/treatment operations prior to disposal.
- The HTS coated tape would then be further coated with some kind of passivation/insulation layer. Details about these are not available at present.

3.8 Electrodeposition

This is an electrochemical method whereby dissolved material in an ionized form is uniformly deposited over the substrate maintained at the appropriate polarity. In the literature, no information was found for applying buffer coating over the metal substrate, however, it is assumed here that this technique would work on any suitably textured substrate tape. A process schematic incorporating this electrodeposition method is shown in Figure 11. The major operating steps involved in this scheme are as follows:

- Preparation of precursor salts solution

Initially, dimethyl sulfoxide (DMSO) was used as an organic solvent to dissolve stoichiometric amounts of Y, Ba and Cu nitrates⁽¹⁵⁾. But later on to avoid possible incorporation of sulfur from DMSO in the HTS film, Abolmaali and Talbot replaced DMSO with isopropanol⁽¹⁶⁾. In principle, electrodeposition from both aqueous and non-aqueous solutions should work. However, aqueous solutions are apparently unsuitable because the reduction of water (-1.23v vs. NHE) is kinetically more favorable on most electrode materials (except Hg) than are the alkaline metals (<2.0v vs. NHE). The non-aqueous solution containing precursor salts is prepared using reagent grade chemicals; (e.g. isopropanol, Ba(NO₃)₂, Cu(NO₃)₂, 2.5 H₂O, and Y(NO₃)₃ · 6 H₂O). Initially, the nitrate salts are dissolved in an acidified (with dilute HNO₃ solution) deionized water. The resulting aqueous solution is then further diluted using isopropanol to provide necessary concentration of each metal nitrate. This solution is then used as an electrolyte in the electrolytic cell.

- The suitably textured substrate tape is introduced into the electrolytic cell at a predetermined rate. The nitrate precursor solution is also filled in this cell. The electrolyte solution will require recirculation system so that buildup of undesirable species in the electrolyte can be controlled at or below the acceptable level by taking a slip stream. This slip stream will need to be appropriately

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Figure 11. Conductor Coating Scheme Following Electrodeposition Method

treated prior to recovery and reuse or disposal.

- The coated tape then enters the dryer where at about 150°C, the adsorbed water is vaporized and some of the hydroxide forms in the deposited film [e.g. $\text{Cu}(\text{OH})_2$ and some $\text{Y}(\text{OH})_3$ start decomposing to the respective oxide forms. For $\text{Ba}(\text{OH})_2$ the decomposition to oxide form needs a higher temperature (about $\geq 560^\circ\text{C}$).
- The off-gases from the dryer will also need to be treated to remove contaminant species (such as nitrogen oxides, acetone, alcohol vapors, etc.) before being disposed off in an environmentally acceptable manner.
- The tape coming out of the dryer will be then wound on a spool for subsequent thermal treatment in a batch or semi-batch mode. Either a number of such spools will be heat-treated simultaneously or each one will undergo such treatment in an assembly line type of a setup.
- In the first stage of thermal treatment the spools containing coated and partially oxidized tapes undergo further decomposition in a O_2/N_2 (low $p\text{O}_2$) atmosphere. Required epitaxial structure of the YBCO phase would also develop during this phase.
- In the second stage of the thermal treatment, the spools containing coated tapes are now cooled from 500°C to about room temperature at the prescribed rate in the O_2 -containing atmosphere.
- Off-gases from both phases of the thermal treatment will be collected and treated appropriately prior to disposal or recycle.
- The cooled spools can either go to the stage where outer passivation/insulation layer is applied (this is not shown here as no information is available on the type of material and what method of application to use) or it can be taken to the front of the electrolytic cell to apply another layer of the HTS material by this electrochemical method. According to Abolmaali⁽¹⁶⁾, the film produced from the successive depositions yielded a more contiguous film upon oxidation in their laboratory work.

3.9 Electrophoresis

Of all the candidate options being considered here, this is probably the only option that has been tested in producing a kilometer lengths of fully superconducting fiber at rates up to ~ 1 meter/min. Actually, this is a powder coating technique and does not need high energy beams/ions as in a physical method or precursor salts and complex chemical reactions as in non-physical/chemical methods. Woolf and co-workers have tested this concept starting with the silver wire at the General Atomics-(GA)⁽⁷⁾. However, they did not start with the textured metal substrate tape, and therefore, it is believed that improved values of J_c in the finished product probably can be achieved if one starts with a thinner but pre-textured substrate tape. This slightly modified version of their processing scheme is shown here in Figure 12. The major operating steps involved in this scheme are as follows:

- Preparation of YBCO (HTSM) slurry
 - Superconducting powder material of composition $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ is synthesized via solid-state reaction of Y_2O_3 , BaCO_3 and CuO . Each of these oxides can be purchased as a relatively pure and cheap chemical. On calcination, the mixture of oxides produces a single phase material. This is then pulverized/ground to a particle size of $0.5\text{-}10\mu$ and then suspended in a non-aqueous liquid. General Atomics' published information does not say what this non-aqueous liquid would be, however, any nontoxic organic solvent that can maintain a stable YBCO (HTSM) slurry from room temperature to working (application) temperature should work
- In the electrophoresis chamber #1, the suitably textured substrate tape is continuously fed. The

Figure 12. Conductor Coating Scheme Following Electrophoresis Method

YBCO slurry contained in this chamber under electrophoretic forces forms a coating on the continuously vertically moving tape. By adjusting the speed of the tape and slurry concentration as well as electrophoretic force parameters the required film thickness can be achieved. Also, some kind of recycle loop will be needed to maintain the slurry characteristics (composition, concentration, flow properties and surface properties) at the desired levels. A slip stream from this slurry recycle loop may be treated as required and then disposed of or reused.

- The coated tape is then introduced into the sintering furnace #1 which is maintained at 950-1030°C under O₂/N₂ (low pO₂) atmosphere. According to the GA information, a residence time of about 1 to 30 minutes is needed for the coated tape to undergo complete sintering and oxidation.
- Preparation of silver slurry
Slurry of fine silver (Ag) powder is prepared in the non-aqueous solvent/liquid. Most likely the same liquid as used in YBCO/HTSM slurry or a similar liquid can be used. Information on the size of the fine Ag powder or the non-aqueous liquid used in the GA work⁽⁷⁾ is not available.
- The sintered superconductor coated tape enters the electrophoresis chamber #2 where the silver powder from the silver slurry is electrophoretically applied. Again, similar to YBCO slurry a recycle loop may be needed to maintain the characteristics of the silver powder slurry at the desired level.
- Following silver deposition, the silver coating is then sintered in a furnace operating in low O₂ atmosphere at about 850-950°C. The residence time required based on the GA work ranges from 0.2 to 10 minutes. Off-gases from this sintering furnace are also led to the recovery/treatment section where they are combined with the similar off-gases from furnace #1 or kept separate (depends on the non-aqueous solvent as well as kind of treatment) for the necessary recovery/treatment operations. Also the sintered wire is then wound on a take-up spool for further heat treatment.
- Either a single spool or number of such spools with the silver-coated HTS-coated tape are further oxidized in a chamber where necessary O₂ atmosphere is maintained and the temperature is kept around 400-500°C. According to the GA literature⁽⁷⁾ this activity needs about 1-3 days so it is better to carry it out in a batch mode. After heating the spools are cooled to room temperature.
- Whether the silver-coated tape that comes out of the above scheme would need an additional layer of outer passivation/insulation material was not addressed by GA. So we have not shown this step in our scheme here.

From the process flow schemes given here for these nine candidate options, the similar schemes for the other options (not discussed here) can be easily developed. Usually for the physical methods, the difference will be found in a mechanism through which the energy necessary for vaporizing and condensing (either the HTSC material on a suitable substrate or buffer material on a metal substrate) is imparted. For the chemical methods, the difference will most likely be in the precursor salts used for coating and in related thermal treatment steps. In summary, the schemes for the other methods for preparing HTSC material on a continuous scale can be easily put together from what is discussed here by using necessary combinations. Similarly, starting material in each of these process flow schemes is assumed to be some suitably textured substrate which can be prepared using either RABiTS or IBAD techniques.

4.0 Process Evaluation

To address the potential scale-up issues for the most promising options, one needs to evaluate all of these candidate options first based on some selected parameters. Systematic and extensive evaluations of the candidate manufacturing processes to produce long lengths of coated conductor wires/tapes are not available in the literature. Paranthaman at ORNL⁽⁶⁾ and Phillips at Bell Lab⁽¹⁷⁾ have attempted such evaluations on a limited scope. Phillips' review concentrated on selecting the suitable substrate for

subsequent deposition of high-temperature superconducting thin films. For substrate selection, Phillips' review considered the following criteria as important ones:

- Chemical Compatibility
- Thermal Expansion Match
- Surface Quality
- Substrate Cleanliness
- Substrate Homogeneity
- Substrate Thermal Stability
- Need for Buffer Layer(s)

However, Phillips did not discuss the candidate options to achieve desired characteristics for the currently considered substrates.

Paranthaman's⁽⁶⁾ review is probably the first one that has attempted to evaluate each candidate option for HTS application with an objective to determine their potential regarding production of long-length conductors. In his review, he included the following criteria:

- For Buffer (Barrier) Layer
 - Smoothness and Continuity
 - Bi-Axial Alignment
 - Thermal Expansion Mismatch with Substrate and Superconductor
 - Chemical Stability in Low pO_2 Atmosphere
 - Lattice Mismatch with Substrate
- For Physical/Chemical Deposition Techniques
 - Control of Film Stoichiometry
 - Deposition Rate
 - Ability to Cover Large Area
 - Surface Quality of Film

In his evaluation, he included the following candidate techniques for processing of long-length HTS conductors.

- Physical Vapor Deposition Techniques
 - Sputter Deposition
 - Electron Beam Evaporation
 - Flash Evaporation
 - Ion-Beam Assisted Deposition
 - Molecular Beam Epitaxy
 - Pulsed Laser Ablation
- Solution Growth Techniques
 - Metal Organics and Chemical Vapor Deposition
 - Sol-Gel
 - Metal Organics Decomposition
 - Electro Deposition
 - Aerosol (Spray) Pyrolysis

- Powder Deposits
 - From Powder Suspension/Slurries Using Spin-Casting/Dip-Coating/Screen Printing
 - Electrophoresis

As a result of his evaluation, Paranthaman identified the following techniques as promising ones without ranking them:

- Pulsed Laser Deposition
- MOCVD
- E-Beam Evaporation
- MOD
- Sol-Gel Processing

Using these two studies as a guide and nine process flow schemes described earlier as a basis, a list of important parameters was prepared. The preliminary list was then given to various experts in the field for review. The comments and suggestions received from these experts were then incorporated into a final list. This final list is shown in Table 1.

In Table 1, the important parameters are developed for each major component of the finished HTS conductor. For each of these components, the parameters are further divided into chemistry and materials related; and engineering and environmental related parameters. Even though the candidate options are not developed to the extent that adequate information about each major parameter can be obtained, the idea in compiling such an exhaustive list was that when fully developed, each option would have to address these concerns/issues to be a successful commercial choice.

Based on our literature search, it was found that the quantitative data for only a very few parameters were available. Hence, it was decided to use the available quantitative data for evaluating the relative merit/demerit of the candidate option using multi-attribute analysis. Whereas the parameters for which quantitative information was not available we decided to provide a semi-quantitative or qualitative evaluation.

4.1 Multi-Attribute Analysis

Multi-attribute analysis involves the use of an importance rating and a utility scheme to determine the best of several alternatives⁽¹⁸⁾. An additive utility model was used for this analysis, in which the particular option's overall merit/utility, U_o , for any combinations of outcomes for n selected attributes ($x_1, x_2, \dots, x_n$) can be expressed as:

$$U_o = \sum_{i=1}^n w_i \cdot U_i(x_i)$$

where:

w_i = weight (scaling) factor for i th attribute, and

$U_i(x_i)$ = utility of the outcome x_i for i th attribute.

A utility function $U_i(x_i)$ was specified such that for each attribute x_i , $U_i(x_i = x_i^{\ell}) = 0$ and

Table 1. Important Parameters for Evaluating Options for Continuous Processing of Coated HTSC Wires/Ribbons

SUBSTRATE		BUFFER		SUPERCONDUCTOR		PASSIVATION/INSULATION COVERING	
Materials Related	Pretreatment Related	Materials Related	Application Process Related	Materials Related	Application Process Related	Materials Related	Application Process Related
<u>Chemistry & Materials Related Parameters:</u>		Compatibility	Smoothness	Compatibility	Film Surface Quality	Compatibility	Smoothness
Compatibility	Rolling Characteristics	Availability	Continuous/ Semi-Continuous	Precursor Availability	Large-Area Coverage	Availability	Continuous/ Semi-Continuous
Mechanical Properties	Texture/ Orientation	Thermal Expansion	Biaxially Aligned	Chemical Stability	Deposition Rate	Mechanical Properties	Coating Thickness
Availability	Annealing	Chemical Stability	Deposition Rate	Cost	Coating Thickness	Cost	Reduction in J_c
Cost	Surface Roughness	Lattice Mismatch	Coating Thickness	Thermal Expansion	Continuous/ Semi-Continuous	Thermal Expansion	
Thermal Expansion	Grain Boundary Characteristics	Need for Multi-Layers	Material Utilization	Lattice Mismatch	Film Stoichiometry	Oxidation Resistance	
Magnetic Properties		Need for More Than One Buffer		Diffusion Barrier	Texture/Orientation	Electrical Properties	
		Cost			Achievable J_c , J_e Values		
		Diffusion Barrier			Material Utilization		
		Oxidation Resistance					
<u>Engineering & Environmental Based Process Parameters:</u>							
	Process Severity		Process Severity		Process Severity		Process Severity
	Process Complexity		Process Complexity		Process Complexity		Process Complexity
	Energy Needs		Energy Needs		Energy Needs		Energy Needs
	Controllability		Controllability		Controllability		Controllability
	Automation		Automation		Automation		Automation
	Reproducibility		Reproducibility		Reproducibility		Reproducibility
	Cost		Cost		Cost		Cost
	Current Status/ Development Needed		Environmental Acceptability		Environmental Acceptability		Environmental Acceptability
	Scale-up Potential		Safety		Safety		Waste Management
			Waste Management		Waste Management		Current Status/ Development Needed
			Toxicity & Health Hazards		Toxicity & Health Hazards		
			Corrosion		Corrosion		
			Current Status/ Development Needed		Current Status/ Development Needed		
			Scale-up Potential		Scale-up Potential		

$U_i(x_i = x_i^h) = 1.0$. In other words, the worst outcome $(x_i = x_i^l)$ for each attribute was assigned a utility of zero and the best outcome $(x_i = x_i^h)$ was assigned a utility of one. The shape of the utility function was constructed to give more emphasis to the regions closer to the worst and best cases. This function can be chosen as:

$$U_i(x_i) = 1 - \sqrt{1 - X_i^2}$$

where

$$X_i = \frac{x_i - x_i^l}{x_i^h - x_i^l}$$

If $U_i = 1.0$ turns out to be the least preferred utility/merit then the function can be redefined as:

$$U_i(x_i) = \sqrt{1 - X_i^2}$$

This method was successfully used in the past at the University of Tennessee Space Institute (UTSI) in selecting the best anion-exchange resin for desulfurization/dechlorination application out of various candidate resins based on each resin's equilibrium capacity, cycle efficiency, solution concentration and cost of resin^(19,20). In UTSI's study for the resin evaluation, the overall utility, U_o calculated using this approach was adequate in selecting the best resin as well as ranking the others.

This multi-attribute analysis technique was applied to the following parameters for which quantitative information was available in the literature:

- Process Severity (Temperature and Pressure)
- Coating Thickness for HTS Material
- Deposition Rate for HTS Material
- Toxicity and Health Hazards
- Achieved Maximum J_c Value
- Cost of Chemicals and Material Utilization Efficiency

Analysis results for each of these parameters are as follows:

4.1-1 Process Severity

The severity of the process depends mainly on the processing temperature and pressure at which it is conducted. The multi-attribute analysis for the severity is calculated on the basis of deviations in temperature and pressure of the candidate process from room temperature and atmospheric pressure, respectively. A linear form of function was used for comparison because any energy required to operate the candidate process would be directly proportional to these deviations. The individual multi-attribute parameters are calculated separately for the temperature and pressure and are later added together to give a combined parameter for the process severity. The approach and data used for the candidate options are as follows:

• Data Used:

Options	T_{op}^* (°C)	P_{op}^* (mm Hg)
E-Beam	740	10^{-5}
SOL-GEL (a)	150-250	760
MOCVD	600-850	1-10
PLD	800	0.2
MOD	200-400	760
CVD	750-950	20
Aerosol/Spray Pyrolysis	600-800	760
Electrodeposition	25	760
Electrophoresis	950-1030	760

* From process flow sheets given in Figures 4-12 corresponding to the respective HTS coating operation.

(a) Based on private communication from Dr. M. Paranthaman, ORNL, October 30, 1997.

- Assumptions Made: In order to determine the lowest severity factor possible, for a range of temperature and pressure the temperature closer to room temperature and pressure closer to the atmospheric pressure are used.

- Definitions of the Equations Used for Comparison:

for Temperature Severity $x_i = |T_i - T_{RT}|$

for Pressure Severity $y_i = \log(P_i)$

where $T_{RT} = 25^\circ \text{C}$, T_i is in $^\circ \text{C}$ and P_i is in mm Hg

$$X_i = \frac{x_i - x_i^\ell}{x_i^h - x_i^\ell} \quad \text{where} \quad x_i^\ell = 0 \quad \text{and} \quad x_i^h = 925^\circ \text{C}$$

$$Y_i = \frac{y_i - y_i^\ell}{y_i^h - y_i^\ell} \quad \text{where} \quad y_i^\ell = -5.0 \quad (\text{corresponding to } P_i = 10^{-5} \text{ mm Hg})$$

$$\text{and} \quad y_i^h = 2.881 \quad (\text{corresponding to } P_i = 760 \text{ mm Hg})$$

$$\therefore Y_i = \frac{y_i + 5.0}{7.881}$$

$$\text{For Temperature Severity} \quad U_i^T = \sqrt{1 - X_i^2}$$

$$\text{For Pressure Severity} \quad U_i^P = 1 - \sqrt{1 - Y_i^2}$$

For Overall Severity

$$U_i = \frac{U_i^T + U_i^P}{\left(U_i^T + U_i^P \right)_{\max}}$$

$$\text{where } \left(U_i^T + U_i^P \right)_{\max} = 2.0$$

Table 2
Temperature Severity

Options	T_{op} (°C)	x_i	X_i	U_i^T
E-Beam	740	715	0.77	0.63
SOL-GEL	150	125	0.13	0.99
MOCVD	600	575	0.62	0.78
PLD	800	775	0.84	0.55
MOD	200	175	0.19	0.98
CVD	750	725	0.78	0.62
Aerosol/Spray Pyrolysis	600	575	0.62	0.78
Electrodeposition	25	0	0.00	1.00
Electrophoresis	950	925	1.00	0.00

Table 3
Pressure Severity

Options	P_{op} (mm Hg)	y_i	Y_i	U_i^P
E-Beam	0.00001	-5.0	0	0.00
SOL-GEL	760	2.881	1.0	1.00
MOCVD	10	1.0	0.76	0.35
PLD	0.2	-0.699	0.55	0.16
MOD	760	2.881	1.0	1.00
CVD	20	1.301	0.80	0.40
Aerosol/Spray Pyrolysis	760	2.881	1.0	1.00
Electrodeposition	760	2.881	1.0	1.00
Electrophoresis	760	2.881	1.0	1.00

The calculated values of the temperature severity, U_i^T , and the pressure severity, U_i^P , are given in Tables 2 and 3 respectively. The combined attribute/merit for the process severity calculated from these values U_i^T and U_i^P are given in Table 4 for the candidate options.

Table 4
Combined Attribute/Merit Based on Process Severity for Candidate Options

Options	$U_i^T + U_i^P$	U_i
E-Beam	0.63	0.31
SOL-GEL	1.99	0.99
MOCVD	1.13	0.56
PLD	0.71	0.35
MOD	1.98	0.99
CVD	1.02	0.51
Aerosol/Spray Pyrolysis	1.78	0.89
Electrodeposition	2.00	1.00
Electrophoresis	1.00	0.50

4.1-2 Cost of Raw Materials and Material Utilization Efficiency

The options being evaluated for manufacturing of long-length coated conductors use various types of raw materials ranging from exotic metal organics compounds to simple metals. Similarly, all the raw materials, either precursors or constituents of YBCO itself are utilized to different extents in producing a layer of YBCO over the buffer/metal substrate composite. To quantitatively evaluate both these parameters together, the following approach was used:

- It was assumed that the cost of YBCO produced from constituents or from precursors will be significantly higher than the costs of buffer, metal substrate and/or solvents/carrier materials used in the processing. In other words, the chemical cost of producing YBCO from its raw materials would be a major cost as far as the cost of manufacturing of the coated conductors is concerned.
 - Costs of ingredients to produce a unit weight (gm) of YBCO strictly follows the stoichiometry. This means that to produce 1 mole of $\text{YBa}_2\text{Cu}_3\text{O}_7$ one would need 1 mole of Y-compound, 2 moles of Ba-compound, and 3 moles of Cu-compound.
- a. Regarding material utilization during coating application, all the vapor phase transport processes excluding MOCVD (e.g. PLD, E-Beam and CVD) were assumed to have a utilization efficiency of 15%. This value was determined based on the Hammond's work utilizing E-beam technique for YBCO deposition onto the IBAD prepared substrate⁽⁹⁾. Here the efficiency of 15% means that only 15% of the chemicals were utilized in coating the substrate/buffer composite and other 85% being lost to chamber walls or internals or to exhaust streams. For MOCVD, based on the discussion with Dr. Alex Ignatiev of the University of Houston, a typical representative value of 35% for the more efficient vertical chamber configuration was assumed⁽⁵⁹⁾. Although according to him in their experience, they have calculated such efficiency to vary from 30% to 45% for the vertical configuration and 25 to 30% for the horizontal configuration of the MOCVD chamber. For processes involving liquid phase transport or slurry phase transport (e.g. Sol-Gel, MOD, electrodeposition and electrophoresis) the utilization efficiency was assumed to be 85%. In this case the loss of 15% was assumed to be caused by the removal of about 15% material from the recirculation loop to control the buildup of the undesirables, and due to some vaporization losses from the coating chamber, leaks from pumps, flanges, pipe connections and other handling losses.

- Lastly, the raw materials costs were available from the chemical supplier's catalogue (Alfa-AESAR Catalogue, 1995-96 Issue, Johnson Matthey Catalog Company, Inc., Ward Hill, MA) on different shipment weight basis. All of them were then converted to a kilogram basis using the following power factor method.

According to this method,

$$C = \infty R^f - b$$

where C = Cost of a chemical in \$/kg

R = Shipment quantity for which the price is being quoted, and

∞, b = Constants

Knowing the costs of a given chemical for two different shipment quantities, one can determine ∞ and β and then using the above empirical equation can scale-up or down the cost of that chemical on a consistent basis.

The cost in dollars per gram of producing one mole (or 666.2 gms) of YBCO from respective raw materials for different candidate options were calculated using above methodology. The resulting values are reported in Table 5. Using these cost values and a utilization efficiency of 85% for the liquid/slurry phase transport system and 15% to 35% for the appropriate vapor phase transport system, the effective costs of producing YBCO coating were calculated. These costs are given in Table 6.

Using these effective costs, the multi-attribute analysis was applied to determine the attribute/merit for various candidate options based on the cost of raw materials and material utilization efficiency. For that, the parameter x_i was calculated using a logarithmic scale to accommodate wide ranges in the values of the effective costs. Other values were taken as:

$$x_i = \log (\text{effective cost})$$

$$x_i^{\ell} = \log [0.2] = -0.699 \text{ and}$$

$$x_i^h = \log [200] = 2.301$$

$$\therefore X_i = \frac{x_i - x_i^{\ell}}{x_i^h - x_i^{\ell}} = \frac{x_i + 0.699}{2.301 + 0.699} = \frac{x_i + 0.699}{3}$$

and $U_i = \sqrt{1 - X_i}$

The resulting values of U_i for different options are given in Table 7.

Table 5
Estimated Cost of Producing YBCO from Respective Raw Materials for Candidate Option

<i>Option</i>	<i>Raw Material Involved</i>	<i>Raw Material Price \$/gm</i>	<i>Calculated Cost of Producing YBCO \$/gm</i>
E-Beam	Y BaF ₂ Cu	2.17 1.16 2.09	1.50
PLD and Electrophoresis	Y ₂ O ₃ BaCO ₃ CuO	3.65 1.28 0.24	2.08
MOCVD	Y(THMD) ₃ Ba(THMD) ₂ Cu(THMD) ₂	7.50 6.00 6.00	27.89
SOL-GEL	Y-isopropoxide Ba-isopropoxide CuO	6.62 4.34 0.24	6.06
CVD	YCl ₃ BaI ₂ ·2H ₂ O CuCl	2.13 5.50 2.11	8.61
Aerosol/Spray Pyrolysis and Electrodeposition	Y(NO ₃) ₃ Ba(NO ₃) ₂ Cu (NO ₃) ₂ ·6H ₂ O	1.00 0.77 0.54	1.74
MOD	Y - acetate Ba - acetate Cu - acetate	1.08 2.30 3.39	4.98

4.1-3 Deposition Rate and Overall Thickness for YBCO

The physical dimensions of the coating chamber used in applying the HTS layer(s) over the textured substrate tape will be related to the HTS deposition rate as well as to the desired overall thickness of the HTSC material. These dimensions in general will be inversely proportional to the deposition rate and will be directly proportional to the thickness of the layer being developed inside that chamber. As a result, a combined parameter of "t/R" where t is thickness in Å and R is a deposition rate in Å/sec, was defined for multi-attribute analysis. Literature reported data were used to calculate this parameter for various candidate options. The data used, equations defined for comparison and the resulting values of the attribute/merit are as follows:

Table 6
Effective Cost of Producing YBCO Layer for Candidate Options

<i>Option</i>	<i>Estimated Cost of YBCO (\$/gm)</i>	<i>Material Utilization Efficiency (%)</i>	<i>Effective Cost of YBCO (\$/gm)</i>
E-Beam	1.50	15	10.01
PLD	2.08	15	13.89
MOCVD	27.89	35*	79.69
SOL-GEL	6.06	85	7.13
CVD	8.61	15	57.40
Aerosol/Spray Pyrolysis	1.74	85	2.04
MOD	4.98	85	5.85
Electrodeposition	1.74	85	2.04
Electrophoresis	2.08	85	2.45

* According to private communication with Dr. Alex Ignatiev (Ref. 59)

Table 7
Multi-Attribute Analysis for Cost of Chemicals and Material Utilization Efficiency Parameters

<i>Option</i>	<i>Effective Cost (\$/gm)</i>	x_i	X_i	U_i
E-Beam	10.01	1.000	0.57	0.82
SOL-GEL	7.13	0.853	0.52	0.86
MOCVD	79.69	1.901	0.87	0.50
PLD	13.89	1.143	0.61	0.79
MOD	5.85	0.767	0.49	0.87
CVD	57.40	1.759	0.82	0.57
Aerosol/Spray Pyrolysis	2.04	0.310	0.34	0.94
Electrodeposition	2.04	0.310	0.34	0.94
Electrophoresis	2.45	0.389	0.36	0.93

- **DATA USED:**

Options	Thickness of Superconductor Coating, t (Å)	Reference Number	Superconductor Deposition Rate, R (Å/s)	Reference Number
E-Beam	10,000	9	100	9
SOL-GEL	10,000	21	30	22
MOCVD	3,000	23	20	25
PLD	2,000	24	5	26
MOD	3,000	14	25	14
CVD	6,000	11	8.33	11
Aerosol/Spray Pyrolysis	10,000	13	1.389	13
Electrodeposition	N/D	--	N/D	--
Electrophoresis	N/D	--	N/D	--

N/D = Not Determined because of the literature reported poor J_c values.

- Definitions of the Equations Used for Comparison:

$$x_i = \log \left(\frac{t_i}{R_i} \right)$$

$$X_i = \frac{x_i - x_i^\ell}{x_i^h - x_i^\ell}$$

$$\text{where } x_i^\ell = \log \left(\frac{2,000 \text{ Å}}{145 \text{ Å/s}} \right) = \log (13.79) = 1.14 \quad (\text{based on Hammond's paper, ref. 9})$$

$$x_i^h = \log (7,500) = 3.87 \quad \text{arbitrarily chosen}$$

$$U_i = \sqrt{1 - X_i^2}$$

The calculated values of the attribute/merit for the candidate options are given in Table 8.

Table 8
Multi-Attribute Analysis for Thickness
and Deposition Rate of YBCO

<i>Options</i>	x_i	X_i	U_i
E-Beam	2.00	0.31	0.95
SOL-GEL	2.52	0.50	0.86
MOCVD	2.18	0.38	0.93
PLD	2.60	0.53	0.85
MOD	2.08	0.34	0.94
CVD	2.86	0.63	0.78
Aerosol/Spray Pyrolysis	3.86	0.99	0.13
Electrodeposition	N/D	N/D	N/D
Electrophoresis	N/D	N/D	N/D

(N/D = Not Determined because of literature reported poor J_c values).

4.1-4 Achieved Maximum Critical Current Density, J_c (for YBCO film $\geq 1\mu\text{m}$ thick)

The critical current density, J_c , determines the performance of the coated superconductor. The aim is to have a high J_c value exceeding 1.0×10^6 amp/cm² for the superconductor. It is appropriate to consider HTS film of at least 1 micron thickness; and the field (self or applied) to be at least 0.1T, since J_c falls very rapidly with field strength in the low-field region. Similarly, a very thin film (say 1000 Å in thickness) might show a very large J_c , which would not be realized in a practical conductor. The multi-attribute analysis for J_c value is calculated using the literature reported values. These literature reported values were compiled from our initial survey and are given in Table 9. A logarithmic scale is used to calculate the attribute/merit so the J_c 's of the superconductor made by different processes ranging from 10^2 amp/cm² to $>10^6$ amp/cm² can be easily compared. The approach and the data used for the candidate options are as follows:

- Assumption Made:

The highest value of J_c obtained for YBCO film of thickness $1\mu\text{m}$ or greater and in zero field and reported for either single or poly crystals is chosen for analysis. For sol-gel option, the value corresponding to $0.4\mu\text{m}$ thick film was chosen as it was the only value available.

- Definitions of the equations used for comparison:

$$x_i = \log_{10} J_c$$

$$X_i = \frac{x_i - x_i^\ell}{x_i^h - x_i^\ell} \quad \text{where } x_i^\ell = \log(3.6 \times 10^2) = 2.56...(\text{for electrodeposition}), \text{ and}$$

$$x_i^h = \log(6.3 \times 10^6) = 6.80...(\text{for MOCVD})$$

$$U_i = 1 - \sqrt{1 - X_i^2}$$

Table 9
Literature Reported Critical Current Density and YBCO Film Thickness Values as
Function of Different Conductor Coating Techniques

Conductor Coating Technique	Highest J_c Achieved (amp/cm ²)*	YBCO Film Thickness	Remarks	Ref No.
Sol-Gel	2.0×10^5	4000 Å	YBCO on YSZ with (100) Orientation	10
	1.9×10^4	1 μm	TI-1223 on Silver Foil	21
Metal Organics Chemical Vapor Deposition (MOCVD, PE-MOCVD, etc.)	1.0×10^6	(0.1-0.4) μm	YBCO on LaAlO ₃ with (100) Orientation by PE-MOCVD	23
	2.3×10^6	1000 Å	YBCO on LaAlO ₃ with (100) Orientation by MOCVD	27
	$(0.42-5.0) \times 10^6$	(0.15-0.6) μm	YBCO on LaAlO ₃ with (100) Orientation by Photo-Assisted MOCVD	28
	1.4×10^5	~3000 Å	YBCO by LS-CVD/(MOCVD) on Platinum and Amorphous YSZ Prebuffer Layers (Deposited over Hastelloy C-276 Metal Substrate by Sputtering)	29
	6.3×10^6	0.3 μm	YBCO on SrTiO ₃ Single Crystal with (100) Orientation by OT-CVD/(MOCVD)	30
	2.0×10^4	2000-7000 Å	YBCO on Polycrystalline Silver Foils by MOCVD	31
	2.0×10^5 (Unreproducible)	(0.5-1) μm	YBCO on Polycrystalline MgO Substrate by TC-CVD/(MOCVD)	32
	0.36×10^6		YBCO over IBAD substrate, HTS deposition rate = 1 $\mu\text{m}/\text{min}$	55
	1.0×10^6	>1 μm	for >1 μm thick YBCO film on SrTiO ₃ Single Crystal	60
Chemical Vapor Deposition (CVD)	1.0×10^5 (1×10^6 at 10K)		YBCO by RF Plasma-Enhanced CVD over Ca-stabilized ZrO ₂ using Solution of Metal Nitrates	56
	(1×10^4 at 55K)		Bi-based 2201, 2252 and 2223 on Sapphire using Metal Halides and Plasma-Enhanced CVD Technique	56
	(1.7×10^4 at 4K)		Bi-based HTS on MgO by Thermal CVD without Post Annealing	56
	0.7×10^5	1 μm	YBCO over IBAD sample, 1 μm thick HTS film over 3.0 mm x 10 mm sample	57

Table 9 (continued)

Conductor Coating Technique	Highest J_c Achieved (amp/cm ²)*	YBCO Film Thickness	Remarks	Ref No.
Metal Organics Decomposition (MOD)	3.9x10 ⁵	(0.5-2) μm	YBCO on SrTiO ₃ with (100) Orientation by Dipping Pyrolysis (D-P) Process	33
	1.0x10 ³ (1x10 ⁴ at 4K)	1 μm	YBCO by Spin-Coating on Single Crystal of YSZ Using TFA Precursors	34
	(5x10 ⁵ at 4K)	--	YBCO by Spin-Coating on Single Crystal of SrTiO ₃ with (100 and 110) Orientations Using TFA Precursors	34
	>5.0x10 ⁶	700-2500 Å	YBCO by Spin-Coating on Single Crystal of LaAlO ₃ with (001) Orientation Using TFA Precursors	14
	1.0x10 ⁶	~1 μm	YBCO by TFA process, film thickness ~1 μm on LaAlO ₃ Single Crystal	61
Electrodeposition	3.6x10 ² (4x10 ³ at 4K)	5 μm	YBCO on 9.5 mol % Y ₂ O ₃ Stabilized Cubic Zirconia with (100) Orientation Using Nitrates	35
	(3.96x10 ³ at 4K)	2.5 μm	YBCO on MgO Single Crystal with (100) Orientation Using Nitrates (under constant potential)	15
	(5.1x10 ³ at 4K)	2.5 μm	Same as above (under pulsed potential)	15
	(5x10 ² at 4K)	--	YBCO on Nickel Strip/Wire and Silver Wire Using Nitrates	15
	2.0x10 ⁴	~1 μm	TBCCO on Silver-Coated SrTiO ₃ Single Crystal with (100) Orientation Using Nitrates (under constant potential)	15
	5.6x10 ⁴	~1 μm	Same as above (under pulsed potential)	15
Aerosol/Spray Pyrolysis	3.0x10 ⁴	~1 μm	YBCO on Polished MgO Substrate Using Aqueous Nitrates	13
Electrophoresis	(1.0-2.0)x10 ³	75 μm	Silver-Coated (Sheathed) YBCO on Nickel Alloy Wire	7
Co-evaporation (E-Beam)	>1.0x10 ⁶	~2000 Å	YBCO on SrTiO ₃ (100), LaAlO ₃ (100) and KTaO ₃ (100) Single Crystals, by Co-Evaporation of Y, Cu, and BaF ₂ , up to 1 μm thick film	36
	>1.0x10 ⁶	~0.6 μm	YBCO on LaAlO ₃ (100) Single Crystals by Co-Evaporation of Y, Cu and BaF ₂ , up to 0.4 μm thick film	37
	>1.3x10 ⁶	~2500 Å	YBCO over CeO ₂ /Sapphire (1102) by Resistive Heating of Y, Ba and Cu from W-boat, 2500 Å thick HTS film and 100 Å - 1 μm thick buffer layer	38
	1.0x10 ⁶	~5 μm	YBW by Ex-situ BaF ₂ process, film thickness ~5 μm on SrTiO ₃ Single Crystal	62

Table 9 (continued)

Conductor Coating Technique	Highest J_c Achieved (amp/cm ²)*	YBCO Film Thickness	Remarks	Ref No.
Pulsed Laser Ablation (PLA/PLD)	(4-5)x10 ⁶	1000 Å	YBCO over SrTiO ₃ (100) Single Crystals, 1000 Å thick film	39
	>1.0x10 ⁶	6.4 μm	YBCO over CeO ₂ /YSZ/Hastelloy C-276, YSZ by IBAD, 0.065-6.4 μm thick HTS film	3, 40
	~4.0x10 ⁶	2000 Å	YBCO over SrTiO ₃ (100) Single Crystals, 2000 Å thick film at 145 Å/sec deposition rate	41
	2.5x10 ⁵	1 μm	YBCO over YSZ (by IBAD)/Hastelloy C-276, 1 μm thick HTS film at 5Å/sec deposition rate	42
	(2-3)x10 ⁶	1500 Å	YBCO over SrRuO ₃ /Pt/MgO (100) Single Crystals, HTS - 1500 Å thick, Pt - 500 Å thick, SrRuO ₃ - 2000 Å thick	43
	4.0x10 ⁶	2000 Å	YBCO over SrTiO ₃ /MgO (100) Single Crystals, HTS film 2000 Å thick	24
	1.0x10 ⁵	1600 Å	YBCO over YSZ/Pt/Ni-alloy, YSZ by IBAD, 1600 Å thick HTS film	44
	6.0x10 ⁵	0.4 μm	YBCO over YSZ (by IBAD)/Haynes 230 (0.6 mm thick)	45
	~2.0x10 ⁶	~1 μm	YBCO over SrTiO ₃ (100) Single Crystals 1 μm thick HTS film	46, 47
	(1.5-4.3)x10 ⁵	1 μm	YBCO over YSZ/Hastelloy C-276, short samples to 1 meter long sample, YSZ by PLD; 1 μm thick HTS film	48
	0.8x10 ⁵	1 μm	YBCO over RABiTS Ni, 1 μm thick HTS film	49
	(0.2-3)x10 ⁶	--	3x10 ⁶ on SrTiO ₃ Single Crystal 1x10 ⁶ on Ni with YSZ by IBAD 4x10 ⁵ on YSZ Ribbon with YSZ by IBAD 2x10 ⁵ on YSZ Ribbon	50
	1x10 ⁶	--	YBCO on SiO ₂ and MgO Single Crystals, and Zr foil	51
	1.3x10 ⁶	--	YBCO on CeO ₂ /YSZ/Hastelloy 242, YSZ by IBAD	52
	0.712x10 ⁵	--	YBCO on YSZ/CeO ₂ /RABiTS Ni	53
	1.5x10 ⁵	~3 μm	YBCO over YSZ/Ni-alloy without ion beam assistance in deposition of YSZ, 3 μm thick HTS film, 1-2 μm YSZ thickness, outer layer of Ag by sputtering, tape width = 10mm, length = 1 m, HTS deposition rate = 0.5 μm/min	54

* J_c reported at 77K and under no field

• DATA USED

<i>Options</i>	<i>J_c Achieved x 10⁻⁶ (amp/cm²)</i>	<i>Reference No.</i>
E-Beam	1.0	62
SOL-GEL	0.2*	10
MOCVD	1.0	60
PLD	1.0	3,40
MOD	1.0	61
CVD	0.07	57
Aerosol/Spray Pyrolysis	0.03	13
Electrodeposition	0.056	15
Electrophoresis	0.002	7

*For 0.4 μm thick YBCO film

The calculated values of the attribute/merit based on the achieved J_c values for candidate options are given in Table 10.

Table 10
Multi-Attribute Analysis for Literature Reported Achieved J_c Values for YBCO Film > 1 μm Thick

<i>Options</i>	<i>J_cx10⁻⁶ (amp/cm²)</i>	<i>Log (J_c)</i>	<i>X_i</i>	<i>U_i</i>
E-Beam	1.0	6.0	0.81	0.41
SOL-GEL	0.2	5.30	0.65	0.24
MOCVD	1.0	6.0	0.81	0.41
PLD	1.0	6.0	0.81	0.41
MOD	1.0	6.0	0.81	0.41
CVD	0.07	4.84	0.54	0.16
Aerosol/Spray Pyrolysis	0.03	4.48	0.45	0.11
Electrodeposition	0.056	4.75	0.52	0.14
Electrophoresis	0.002	3.30	0.17	0.01

4.1-5 Toxicity and Health Hazards

The health hazards related with the candidate manufacturing option depend on the toxicity of the raw materials used. The LD₅₀ values (minimum lethal dose at which 50% of the sample population die) of the chemicals associated with the respective process are used as the basis for calculating the attribute/merit parameters for the toxicity possible from the given process.

Since many of the metal organics used as precursors in certain candidate options are prepared on a small scale and are relatively new, the Materials Safety and Data Sheets (MSDS) for such chemicals are

either non-existent or are incomplete. As a result, the analysis for calculating the attribute/merit based on the toxicity parameter is incomplete at present. The approach and data used for the candidate options for which a limited amount of toxicity information is available are given as follows:

- **Data Used**

<i>Options</i>	<i>Toxicity LD₅₀ (mg/kg)</i>	<i>Toxic Compound Considered</i>
SOL-GEL	410	Lanthanum Nitrate Hexahydrate
MOD	11	Barium Acetate
CVD	265	CuCl
Aerosol/Spray Pyrolysis	8.5	Barium Nitrate
Electrophoresis	350	Y ₂ O ₃

- Assumptions Made:

The most toxic substance from the several that are used in the given manufacturing process option is chosen for this analysis.

- Definition of the Equations Used for Comparison:

$$x_i = \log(LD_{50})$$

Based on toxicity of pesticides, the categories considered by the U.S. EPA (Environmental Protection Agency) are:

Highest toxicity = 0-50 mg/kg

Lowest toxicity = >5000 mg/kg

$$\therefore x_i^{\ell} = 1 \text{ mg / kg} \text{ \& } x_i^h = 5000 \text{ mg / kg}$$

$$X_i = \frac{x_i - x_i^{\ell}}{x_i^h - x_i^{\ell}}; \quad U_i = 1 - \sqrt{1 - X_i^2}$$

The calculated attributes/merits for the candidate options for which some data were available are given in Table 11.

Table 11
Multi-Attribute Analysis for Toxicity of Raw Materials/Intermediates
Used in HTSC Manufacturing Option

<i>Options</i>	<i>X_i</i>	<i>U_i</i>
SOL-GEL	0.71	0.3
MOD	0.28	0.04
CVD	0.66	0.25
Aerosol/Spray Pyrolysis	0.25	0.03
Electrophoresis	0.69	0.28

4.2 Subjective Evaluation

As mentioned earlier, the quantitative data for most of the parameters are not yet available. For such parameters, a subjective evaluation was attempted. A scale of 1 to 5 was used where each score represented the following characteristics:

- 1 - Totally (or consistently) favorable/acceptable
- 2 - Frequently favorable/acceptable
- 3 - Variably favorable/acceptable
- 4 - Frequently unfavorable/unacceptable
- 5 -Totally unfavorable/unacceptable

Using above scoring system the following parameters were subjectively evaluated for the candidate options:

- Raw Material Availability and Cost
- Chemical Stability
- Continuous/Semi-Continuous Operation
- Film Stoichiometry
- Large Area Coverage
- Film Surface Quality
- Material Utilization Efficiency
- Process Complexity
- Energy Needs
- Controllability
- Automation
- Reproducibility
- Current Status/Development Needed
- Scale-Up Potential
- Environmental Acceptability
- Safety
- Waste Management
- Corrosion
- Toxicity and Health Hazards

To come up with the appropriate scores for each of the candidate options for the selected parameters help was solicited from the “experts” working in the field of HTS development. Similarly, related literature was also reviewed. External input on the subjective evaluation was received only from the Oak Ridge National Laboratory (ORNL). This is shown in Table 12. The ORNL evaluation seems to emphasize more on the technical performance achieved rather than on the engineering and environmental criteria. An in-house prepared subjective evaluation at UTSI is shown in Table 13.

Comparing the UTSI and ORNL evaluation one can see that UTSI emphasized more on the generic parameters related to the engineering and environmental concerns. Since technical performance related parameters (J_c , deposition rate, thickness etc.) are already separately evaluated in the quantitative evaluation to calculate respective attributes/merits, emphasizing them again would unduly penalize or handicap the given option twice.

Table 12. (ORNL's Evaluation)
Subjective Evaluation of Candidate Options for Manufacturing Long-Length HTS Wires/Tapes

<i>Parameter</i>	<i>Pulsed Laser Deposition(PLD)</i>	<i>E-Beam</i>	<i>MOCVD</i>	<i>Solgel</i>	<i>CVD</i>	<i>Aerosol/Spray Pyrolysis</i>	<i>MOD</i>	<i>Electro- deposition</i>	<i>Electro- phoresis</i>
• Chem. & Mat'l Related									
Raw Mat'l Avail./Cost	3	2	4	4	--	3	2	3	3
Chemical Stability	3	3	3	4	--	3	3	3	3
Cont./Semi-Cont.System	3	2	2	3	--	4	4	3	3
Film Stoichiometry	1	2	3	2	--	2	2	4	4
Large Area Coverage	4	2	3	2	--	3	2	3	3
Film Surface Quality	2	2	3	3	--	4	3	4	4
Mat'l Utilization Efficiency	3	2	3	4	--	4	3	3	4
• Eng'n & Environ.Related									
Process Complexity	3	2	3	3	--	4	3	4	4
Energy Needs	4	3	3	3	--	3	3	4	4
Controllability	2	3	3	3	--	4	3	4	4
Automation	4	2	3	3	--	3	3	3	3
Reproducibility	2	3	3	3	--	4	4	4	4
Current Status/Dev. Needs	3	2	3	3	--	4	3	4	4
Scale-Up Potential	3	2	4	4	--	4	4	4	4
Environ. Accept.	3	3	4	4	--	4	4	4	4
Safety	4	3	3	3	--	3	3	3	3
Waste Management	3	3	4	4	--	4	4	4	4
Corrosion	3	3	3	4	--	4	4	4	4
Toxicity & Health Hazards	3	2	3	3	--	4	4	4	4
TOTAL SCORE =	56	46	60	62	--	68	61	69	70

Explanation: Score of

- 1 - Means totally (or consistently) favorable/acceptable.
- 2 - Means frequently favorable/acceptable.
- 3 - Means variably favorable/acceptable.
- 4 - Means frequently unfavorable/unacceptable.
- 5 - Means totally unfavorable/unacceptable.

TABLE 13 (UTSI'S Evaluation)
Subjective Evaluation of Candidate Options for Manufacturing Long-Length HTS Wires/Tapes

<i>Parameter</i>	<i>Pulse Laser Deposition (PLD)</i>	<i>E-Beam</i>	<i>MOCVD</i>	<i>Solgel</i>	<i>CVD</i>	<i>Aerosol/Spray Pyrolysis</i>	<i>MOD</i>	<i>Electro- deposition</i>	<i>Electro- phoresis</i>
• Chem. & Mat'l Related									
Raw Mat'l Avail./Cost	1	2	4	4	2	1	1	1	2
Chemical Stability	2	3	4	4	2	2	3	2	2
Cont./Semi-Cont.System	3	3	4	3	3	3	3	3	2
Film Stoichiometry	3	3	4	3	4	4	3	4	4
Large Area Coverage	4	3	4	2	4	3	2	2	4
Film Surface Quality	2	2	2	2	4	4	3	4	4
Mat'l Utilization Efficiency	4	4	5	2	4	2	2	3	2
• Eng'n & Environ.Related									
Process Complexity	4	2	4	4	4	4	4	2	2
Energy Needs	4	4	4	4	4	4	3	4	3
Controllability	4	4	4	4	4	4	3	3	3
Automation	4	4	4	4	4	4	3	2	2
Reproducibility	3	3	4	4	4	4	3	3	3
Current Status/Dev.Needs	4	4	4	4	4	4	4	4	3
Scale-Up Potential	4	3	3	4	4	3	3	4	3
Environ. Accept.	2	4	4	4	3	3	4	2	2
Safety	2	4	4	4	4	2	4	2	2
Waste Management	2	4	4	4	4	2	4	2	2
Corrosion	1	3	4	3	4	1	4	2	1
Toxicity & Health Hazards	3	4	4	4	4	2	3	2	2
TOTAL SCORE =	56	63	74	67	70	56	59	53	48

Explanation: Score of 1 - Means totally (or consistently) favorable/acceptable.

2 – Means frequently favorable/acceptable.

3 – Means variably favorable/acceptable

4 – Means frequently unfavorable/unacceptable.

5 – Means totally unfavorable/unacceptable.

Subsequently, a composite score was prepared for the subjective evaluation score for each of the candidate options by taking an arithmetic average of the UTSI and ORNL scores. This is shown in Table 14. Next, taking the highest possible score of 95 as x_i^h and the lowest possible score of 19 as x_i^l , multi-attribute analysis was applied to these composite scores. The resulting values of the respective utility/attribute are shown in Table 15.

Table 14
Composite Score for Subjective Evaluation

Candidate Option	ORNL Score	UTSI Score	Composite Score
PLD	56	56	56.0
E-Beam	46	63	54.5
MOCVD	60	74	67.0
SOL-GEL	62	67	64.5
CVD	--	70	70.0
Aerosol/Spray Pyrolysis	68	56	62.0
MOD	61	59	60.0
Electrodeposition	69	51	60.0
Electrophoresis	70	48	59.0

Table 15
Calculated Attribute/Merit Based on Composite Score
From Subjective Evaluation

Option	$x_i = \text{Score}$	$X_i = \frac{x_i - x_i^l}{x_i^h - x_i^l}$	$U_i = \sqrt{1 - X_i^2}$
PLD	56.0	0.49	0.87
E-Beam	54.5	0.47	0.88
MOCVD	67.0	0.63	0.77
SOL-GEL	64.5	0.60	0.80
CVD	70.0	0.67	0.74
Aerosol/Spray Pyrolysis	62.0	0.57	0.82
MOD	60.0	0.54	0.8
Electrodeposition	60.0	0.54	0.84
Electrophoresis	59.0	0.53	0.85

4.3 Preliminary Ranking

Next, the utility/merit values calculated from the quantitative data and subjective evaluation scoring were combined using the following weighting factors, representing case 'A'.

Case - 'A'

Parameter	(W _i) Weighting Factor
Processing Temperature	0.16
Processing Pressure	0.16
Coating Thickness & Deposition Rate for HTSC	0.16
Achievable Maximum J _c Value	0.16
Subjective Evaluation Score ^(a)	0.20
Cost of Chemicals/Material Utilization Efficiency	0.16
TOTAL	1.00

(a) Includes nineteen (19) different parameters for which quantitative data are not available at present.

Using these weighting factors and the merit/utility calculated for each parameter, the overall utility/merit values for candidate options following case 'A' were determined. These values of overall utility/merit are given in Table 16. Because the weighting factors for case 'A' were arbitrarily chosen to establish effect of relative importance of important parameters, two other weight distributions were considered. In addition, scale-up potential being of major concern, the scores given by UTSI and ORNL for this particular criterion in subjective evaluation were also considered to determine the comparison of various options. The resulting values of the calculated overall utility/merit for various options following the case A, B and C as well as respective scores for scale-up potential given by ORNL and UTSI to each of the candidate options, all are given in Table 17. Using these results of sensitivity analysis, the preliminary ranking based on each of the three weight distributions considered here was developed. This preliminary ranking following each case is shown in Table 18.

Based on this sensitivity analysis, the MOD and sol-gel are found to be the two leading options from the solution-growth techniques. Also MOCVD, E-beam, and PLD are found to be very close to each other and representing the physical/vapor growth techniques. All these five options have achieved high J_c values on single crystals that range from 10⁵ to 10⁶ amp/cm². These high J_c values on single crystals at least show their potential of achieving similar values on the textured metallic substrates. Also, the two options of MOD and Sol-Gel are based on the method involving a solution growth technique which should be relatively easy to operate in a commercial system. The scale-up potential for each of them is uncertain (e.g., score between 3 and 4) as enough data and experience of operating reel-to-reel mode are not available at present. For subjective evaluation only two responses (including UTSI's) were obtained and for reliable evaluation, one needs a much wider response and participation including that from the industrial partners working in the HTS wire manufacturing efforts. Since this was not available or possible at this time, an important issue of scale-up potential still remains unanswered, and cannot be used for identifying the leading options.

Table 16

CALCULATED OVERALL MERIT/UTILITY FOR VARIOUS CANDIDATE OPTIONS (CASE "A")*

	CALCULATED ATTRIBUTE/MERIT U_i						
OPTION	Based on Processing Temperature	Based on Processing Pressure	Based on Cost of Chemicals & Matl. Utilization Efficiency	Based on Coating Thickness & Deposition Rate for YBCO	Based on Achieved J_c Value	Based on Subjective Evaluation	Calculated Overall Utility/Merit U_o
E-Beam	0.63	0.0	0.82	0.95	0.41	0.88	0.63
SOL-GEL	0.99	1.00	0.86	0.86	0.24	0.80	0.79
MOCVD	0.78	0.35	0.15	0.93	0.41	0.77	0.63
PLD	0.55	0.16	0.79	0.85	0.41	0.87	0.62
MOD	0.98	1.00	0.87	0.94	0.41	0.84	0.84
CVD	0.62	0.40	0.57	0.78	0.16	0.74	0.55
Aerosol/Spray Pyrolysis	0.78	1.00	0.94	0.13	0.11	0.82	0.64
Electrodeposition	1.00	1.00	0.94	N/D	0.14	0.84	N/D
Electrophoresis	0.0	1.00	0.93	N/D	0.01	0.85	N/D

N/D = Not Determined

* Case A corresponds to equal weights for quantitative parameters (e.g. 0.16 each) and 0.20 for subjective evaluation.

Table 17

SENSITIVITY ANALYSIS FOR OVERALL UTILITY/MERIT VALUES

OPTION	CALCULATED OVERALL UTILITY/MERIT, U_o			SCORE FOR SCALE-UP POTENTIAL *	
	CASE A	CASE B	CASE C	ORNL's	UTSI's
E-BEAM	0.63	0.56	0.41	2	3
SOL-GEL	0.79	0.79	0.24	4	4
MOCVD	0.63	0.59	0.41	4	3
PLD	0.62	0.55	0.41	3	4
MOD	0.84	0.84	0.41	4	3
CVD	0.55	0.51	0.16	--	4
AEROSOL/SPRAY PYROLYSIS	0.64	0.59	0.11	4	3
ELECTRO- DEPOSITION	N/D	N/D	0.14	4	4
ELECTRO- PHORESIS	N/D	N/D	0.01	4	3

N/D = Not Determined.

* Score of (1) is best and (5) is worst.

CASE A: Equal weights for quantitative parameters (e.g. 0.16 each) and 0.20 for subjective evaluation.

CASE B: Equal weights for quantitative parameters (e.g. 0.20 each) and zero for subjective evaluation.

CASE C: Based only on maximum J_c value achieved for film thickness > 1 μm and on single or polycrystals.

Table 18
Preliminary Ranking Among Various Candidate Options

<i>Option</i>	<i>Based on Case “A”</i>	<i>Based on Case “B”</i>	<i>Based on Case “C”</i>
E-Beam	4	4	1
SOL-GEL	2	2	2
MOCVD	4	3	1
PLD	5	5	1
MOD	1	1	1
CVD	6	6	3
Aerosol/Spray Pyrolysis	3	3	5
Electrodeposition	--	--	4
Electrophoresis	--	--	6

Lastly, a word of caution is being given to all readers of this report and that is that the above preliminary rankings have been developed from the literature values for various parameters and candidate options that were made available to us. Since a significant portion of the HTSC development work is being carried out in a proprietary fashion, some of the proprietary data were not available to us. Similarly, the emerging methods and techniques such as Liquid Phase Epitaxial (LPE) growth and non-contact heating method for substrate heating to facilitate dual side deposition when sufficiently developed may change some of the relative merits of the candidate options. Such information when it becomes available need to be incorporated in the future revision of this evaluation. Hence, it is possible that the rankings developed here may change in the future. For the owners of related confidential data now they have the knowledge of the methodology that was used here in developing these rankings. So using a similar method and incorporating their own confidential data, they can always estimate the revised ranking to justify whatever they are currently developing or planning to develop in the future!!

5.0 Determination of Manufacturing Parameters

The determining factor in engineering economy for the manufacturing of a long-length coated conductor will be the annual cost of operation divided by the length of quality product produced per year. In other words, candidate options will be compared in terms of their cost of production of a unit length of wire/tape. Of course, the other critical parameters are already described and evaluated earlier. To develop a methodology to generate cost per unit length of tape, the approach reported by Hammond was used⁽⁹⁾.

According to Hammond's approach, the length of the quality tape produced per year is defined as, (S), in terms of the process tape speed with the units of length per time. At normal operation, tape speed in the various manufacturing operations which are carried out in a continuous mode should be the same. In other words, if S_B is speed for the buffer application section and S_H is speed for the HTS application section then S_B should be equal to S_H .

In terms of other process parameters,

$$S = RA/(t w)$$

where R = Deposition Rate (usually in $\text{\AA}/\text{sec}$)
 A = Area of Deposition (usually in m^2)
 t = Thickness of Deposit (usually in $\text{\AA}$)
 w = Width of the Tape Being Deposited (usually in m)

Also, for the same width of tape throughout the process,

$$A = L \cdot N_p \cdot w$$

where L = Deposition Process Length

N_p = Number of Passes the Tape Makes in a Particular Section Per Stage

If the total thickness, t , for the deposit is achieved in a number of stages operating in a series and each stage operating at the same average deposition rate and also has similar chamber dimensions, as well as other operating parameters, then,

$$t = N_s \cdot t_s$$

where N_s = Number of Stages in a Series

t_s = Thickness of Deposit Achieved Per Stage

Again, if the tape width is subsequently sliced into “ m ” equal slices to yield the final product, then the equivalent process speed, S_{eq} is given by:

$$S_{eq} = S \cdot m$$

Incorporating all above possibilities, we would get:

$$S_{eq} = m \cdot S_B = m \cdot S_H$$

$$\text{and } S_B = \frac{R_B L_B N_{p,B} (N_s)_B}{(t)_B}$$

$$\text{and } S_H = \frac{R_H L_H N_{p,H} (N_s)_H}{(t)_H}$$

where L_B = Length of deposition process length per stage in buffer application section
 $(N_p)_B$ = Number of passes made by tape per stage in buffer application section
 $(N_s)_B$ = Number of stages in series in buffer application section
 $(t)_B$ = Overall thickness of deposit achieved in buffer application section
 R_B = Average deposition rate for buffer layer per stage

and similar definitions for the terms involved in S_H .

5.1 Manufacturing Parameters for a Continuous Plant

Using above approach and the available literature, the manufacturing parameters for various candidate processes were estimated. The basic assumptions made in this estimation are as follows:

Manufacturing Capacity = 6000 km/year of quality tape/wire
Tape/Wire Processing Speed = 3 cm/sec
Process Width = 10 cm
m, Number of Post Process Slices = 10
Operation Time = 24 Hours a Day, 7 Days a Week and Throughout Year
Percentage of On-Spec Material Production = 63.4%

At above conditions, if the plant was producing 100% of the time on-spec material then overall capacity would have been 9460 km per year. But by having on-spec material only 63.4% of the time or in other words having a plant available for production only 63.4% of the time, the useful production comes out to be about 6000 km per year. Hence S_{eq} is equal to 9460 km/year and m is equal to 10 slices.

Using the process schematics described earlier and the basic assumptions listed above, the manufacturing parameters (e.g. Values of R , N_p , N_s , L , t , etc.) for the candidate processes were estimated. These values are given in Table 19 along with the similar values reported by Hammond⁽⁹⁾. Parameters for the electrodeposition and electrophoresis options were not developed because the literature reported performance (e.g. J_c values) for these options are not acceptable.

5.2 Preliminary Process Design

Although not attempted at present, the parameters for the identified five candidate options can be used in the future to determine the preliminary size and major specifications for the important components involved in the respective continuous mode HTS wire/tape manufacturing processes. However, until an additional experimental data base becomes available, such a preliminary estimation at present would be rather unreliable and of little use, and therefore was not attempted.

6.0 **Major Concerns/Issues and Datagap for the Promising Candidate Options**

As a result of the process evaluation, the leading candidate options to apply epitaxial buffer and HTS layers are MOD, Sol-Gel, PLD, E-beam, and MOCVD. Similarly, to prepare textured substrate, the only options available at present include RABiTS and IBAD. Enough information for the latter two options is not available in the open literature to compare one with the other. None of these seven concepts (i.e., MOD, Sol-Gel, PLD, E-Beam, MOCVD, RABiTS and IBAD) are developed to the extent where a reliable, commercially viable process can be designed to produce long-lengths of coated conductors in a continuous mode. A significant amount of development work is needed for each of them. Areas of major concerns/issues and significant gaps in the useful data for each of these promising concepts are as follows:

6.1 IBAD Related Technical Issues

Robert Hammond and his co-workers at the Stanford University⁽⁹⁾ have provided a very useful and critical review of the concerns and issues related to this concept. Following list includes some additional concerns.

- Crystalline quality of the IBAD layer that can be achieved.
- Required thickness of the IBAD layer to achieve desired performance (J_c etc.)
- Possible requirement for a buffer layer between the metal substrate and the IBAD layer to prevent chemical diffusion.

Table 19
List of Manufacturing Parameters for Candidate Options

- Basis:**
- Manufacturing Capacity = 6000 km/year
 - Tape Process Speed = 3 cm/s
 - Process Width = 10 cm
 - m (# of Post Process Slices) = 10
 - Plant Operates 24 Hours a Day, 7 Days a Week and Producing On-Spec Material 63.4% of the Time

PROCESS	Hammond's Concept	SOL-GEL	MOCVD	PLD	MOD	CVD	Aerosol/Spray Pyrolysis
<i>Buffer 1</i>	YSZ	LaAlO ₃	CeO ₂	YSZ	LaAlO ₃	LaAlO ₃	LaAlO ₃
Application Method	IBAD	SOL-GEL	E-Beam	PLD	SOL-GEL	SOL-GEL	SOL-GEL
R	2	30	0.667	1.69	30	30	30
L	1.5	1	0.9	3.55	1	1	1
Np	1	1	5	5	1	1	1
Ns	1	4	1	1	4	4	4
t	100	4,000	100	1,000	4,000	4,000	4,000
<i>Buffer 2</i>	None	None	YSZ	CeO ₂	None	None	None
Application Method			E-Beam	PLD			
R			1.167	0.967			
L			0.9	3.1			
Np			10	10			
Ns			4	1			
t			1,400	1,000			
<i>Superconductor</i>	YBCO	YBCO	YBCO	YBCO	YBCO	YBCO	YBCO
Application Method	E-Beam	SOL-GEL	MOCVD	PLD	MOD	CVD	Spray Pyrolysis
R	100	30	20	145	25	8.33	1.389
L	3	1	0.9	0.4	3.6	2.16	2.16
Np	1	1	5	1	1	1	10
Ns	1	10	1	1	1	10	10
t	10,000	10,000	3,000	2,000	3,000	6,000	10,000

R: Deposition Rate (Å °/s)

Np: Number of Passes Per Stage

t: Overall Thickness of Coating (Å °)

L: Length (m)

Ns: Number of Stages in Series

- To coat both sides of the tape uniformly and having multiple-passes of a moving tape in a single chamber pose a significant engineering challenge in designing a vacuum-based reactor system. How to get Ar⁺ ion beam at a precise angle to direct YSZ deposition on Hastelloy substrate so that epitaxial crystallinity can be maintained in such a system for all the passes and at both tape surfaces can be a tremendous challenge.
- Off-gases from such a coating chamber also need to be analyzed to design/develop suitable recovery/treatment/disposal system.
- YSZ or any other suitable buffer material deposited on the walls and other internals may need to be removed periodically to maintain efficient operation. Information needs to be acquired regarding how quickly it builds up and how often it needs to be removed. Similarly, suitable treatment/disposal option for the collected deposits need to be identified also.

6.2 RABiTS Related Technical Issues

Most of the information about this concept is not available in the open literature. Whatever is acquired through personal contacts and newsletter briefings show that the most likely concerns and issues for this concept would include the following:

- **Acceptable Quality of Textured Tape--**
Manufacturing of long-length tapes from Ni-rich alloy material of very small (a few micron) thickness and with acceptable bi-axial texture needs to be demonstrated. Diagnostic and quality control systems that can monitor various parameters on-line need to be developed and tested. Similarly, if splices are made after removing the off-spec material, ways to connect them need to be developed. Again, if this texturization treatment is carried out on-line with the production of the YBCO-coated conductor wire, then a question remains whether rolling and annealing that are necessary for RABiTS can be carried out continuously at few centimeters per second rate. If it is prepared off-site and shipped on a spool, then any degradation in the crystalline nature during the storage and then transportation need to be considered. Whether nickel or other alloy constituents of the tape would oxidize or react with the surrounding atmosphere also need to be evaluated. Smoothness is also a major unsolved problem. In general, textured substrate provides the foundation over which the brickwork of the buffer and YBCO will be laid. So if the foundation is not properly aligned (i. e. textured) the final structure built over it may not have acceptable texture.
- **Annealing Furnace--**
Off-gases from an annealing furnace needs to be analyzed to develop/identify a suitable recovery/treatment/disposal scheme. If annealing duration lasts a few hours a day, then on-line thermal treatment may not be possible, and therefore, an alternative scheme for rolling and annealing may be needed.
- **Recrystallization or Secondary Crystallization of Metal Substrate--**
If the annealing temperature used in initial operations to develop appropriate crystal structure is lower than the temperatures used during applications of suitable buffer material and/or HTS material (such as drying or pyrolysis temperature or post-annealing temperature) then there is a possibility that original metal substrates may recrystallize or undergo secondary crystallization to a different form or size of the crystals and, as a result, anticipated epitaxial structure may not then be achieved.
- **Applicability to Other Metal Substrates--**
So far, limited information is available for pure nickel. But whether using similar rolling and annealing operations, a similar success can be achieved using Ni-rich alloy or copper or silver

or any other suitable metal substrate needs to be demonstrated.

- **Applicability of Buffer Deposition Option--**
So far to our knowledge, PLD and E-beam type physical deposition methods as well as sol-gel type non-physical or chemical deposition method have been tried to deposit layers of suitable buffer material (e.g. YSZ, CeO_2 etc. in case of physical methods and LaAlO_3 in case of sol-gel method) onto rolled nickel-rich alloy substrate to prepare textured substrate by the RABiTS method (see Figures 1 and 2). In case of the chemical method such as sol-gel, satisfactory epitaxial structure is not yet achieved. This raises a major concern of whether a rolled nickel substrate can accept any of the HTS coating options discussed here to provide a textured substrate or is it limited to a physical deposition option only? If it is restricted to only physical deposition option then a potential to reduce overall cost of wire/tape production by using a potentially low-cost, solution-growth based option may not be possible.

6.3 Sol-Gel Related Technical Issues

Sol-gel method is used to apply LaAlO_3 coating over a suitable rolled metal substrate as well as to apply YBCO coating over a suitably textured buffer coated substrate. The concerns and issues in each case will be similar and as a result, here we have listed everything in terms of YBCO deposition. The major technical concerns and issues related to sol-gel based YBCO coating are as follows:

- **Precursors gel/solution related--**
 - Precursors for a buffer layer as well as a YBCO layer are prepared on site or off-site from raw materials and then transformed into a gel/solution form. First, the entire recipe to prepare such a gel/solution is very involved and needs a lot of processing steps. It needs to be simplified. Some of the alternative operations such as distillation and redilution versus handling of a dry product etc. need to be evaluated to reduce the number of operating steps. It is believed that often the precursor gel results in a poor structural form, and organometallic salt containing copper are not easily available. Similarly, organic solvents that are currently being considered do not have adequate solubilities for the precursor metal salts, and therefore, organic solvents with higher solubilities are needed. Also, most of these solvents are costly and may be toxic. Also, the precursor salts (alkoxides) need to be of very high purity and usually are specialty chemicals. As a result they are very costly. Hence, attempts need to be made to use alternative less pure and cheaper salts and evaluate their resulting impact on the performance of the final product.
 - Liquid and gaseous waste/by-products from the preparation of a gel/solution will contain alcohols and organic solvents used in the synthesis. These streams need to be well characterized and appropriate recovery/treatment/disposal schemes need to be identified or developed if necessary.
- **Dip-Coating and Pyrolysis related--**
Of the various options for manufacturing coated conductors, a solution growth-based option such as sol-gel and MOD are believed to be relatively easy to operate, but they have their operational issues/concerns also. One such issue includes the need for multiple stages in a series to achieve the desired film thickness. Since precursor salts gel/solution cost a lot, one cannot afford to have a very large dip-coating tank requiring a large inventory of the gel/solution. On the other hand, having a large number of small tanks would probably save on chemicals, but cost of equipment and other operation costs may increase. Modeling of dip-coating using sol-gel type material is not fully developed since many of the underlying physics and chemistry-related steps are not very well understood. A dip-coating tank is usually maintained at low temperature (most likely close to room temperature) and pyrolyzer following the dip-coating tank is usually maintained at a much higher temperature of 400°C - 800°C . Thus a tape being coated and

pyrolyzed successively goes through a thermal shock causing film to possibly crack. Hence, the major problem that needs resolution is how to avoid cracking the film. Also, it is reported in the literature for solar cells⁽⁵⁸⁾ that if the substrate is drawn too fast from the liquid, then the resulting film will be thicker. For very thin film, one has to draw the substrate at a slow rate. To maintain a given production capacity, this may necessitate having a number of coating tanks in parallel and series. Also, the precursor salts are chemically sensitive and prone to decomposition if not handled properly. Their potential corrosiveness or toxicity/health hazards are not known at present. As a result, one would try to restrict the number of dip-coating tanks to a minimum. Kinetics data for the dip-coating as well as pyrolysis are not available, and therefore, design of an optimum enclosure is not possible at this time. Also, if temperatures for the pyrolyzer can be reduced then the energy costs can be reduced significantly.

- Off-gases from the pyrolyzer and thermal treatment units need to be characterized so that suitable recovery/treatment/disposal systems can be developed/identified.
- Thermal treatment--
Since tape prepared by the sol-gel option would need extensive thermal annealing to complete development of the epitaxial crystalline structure and formation of the YBCO phase, a batch or semi-batch mode of operation is anticipated. However, this particular activity is not optimized yet (time-temperature relationships), and the future engineering design of dryer or cooler would need such information.
- Sol-gel precursor solution will be flowing to each tank or series of tanks in a closed re-circulation mode. As a result of coating, some impurities/undesired products will possibly build up in the loop. To control such a build up, a slip stream will be necessary. This slip stream will have to be appropriately treated prior to its recycle or disposal. Hence, chemistry involved in the coating operation needs to be understood in more detail to address such needs.
- Other simplifying or cost-savings measures that need to be evaluated include:
 - Using N₂ as an inert gas instead of Ar.
 - Using simple and cheaper chemicals to prepare precursors gel/solution.

6.4 MOD Related Technical Issues

The process flow scheme developed/proposed for the MOD option is very similar to the one given for the sol-gel option. As a result, the technical concerns/issues identified and discussed above for the sol-gel case would also apply to the MOD case. The additional issues/concerns are identified mainly because of the use of fluoroacetates in the MOD option, in place of the metal organics precursors for YBCO coating used in the sol-gel option. These additional concerns/issues are as follows:

- Preparation of an organometallic precursor solution containing trifluoroacetates is relatively simpler than the one used for the sol-gel scheme, however, it still needs to be evaluated for possible further simplification using common reagents. It is possible that if organometallic salts are used as carboxylates (e.g. acetates) that some unwanted carbonate such as BaCO₃ may form during the pyrolysis step.
- During the coating and pyrolysis, fluoroacetates are converted to oxyfluorides. As a result, a possibility of starting with the oxyfluorides instead of trifluoroacetates needs to be evaluated.
- Hydrofluoric acid (HF) will be released any time the fluoracetates are heated in the presence of water. This acid is very corrosive and extreme care is usually required in handling such a chemical. Materials of construction used in dip-coating tanks as well as pyrolyzers, thermal

treatment units and duct works need to be selected from the protective materials that can withstand the attack of HF at elevated temperatures and in humid conditions.

- Heat treatment reported in the literature to get acceptable texture for the coated conductor is very complex, involves a lot of steps and needs significantly long time for conversion to oxides, for subsequent annealing and then for cooling. By adjusting the starting organometallic salts to suitable chemical forms, an attempt needs to be made to see whether any of these steps or concerns can be resolved.
- If possible, replace Helium with N_2 as an inert gas.

6.5 MOCVD Related Technical Issues

Chou⁽²⁸⁾, Matsuno⁽²⁹⁾, Wu⁽²⁵⁾ and Leskelä⁽⁵⁶⁾ have provided valuable discussions on MOCVD and related technical issues and concerns. The following list includes some additional concerns and issues.

- Suitable thermal and mechanical properties
Buffer coated textured substrate needs to possess acceptable thermal properties and should not be brittle. This may require additional steps to prepare original metal substrate. Similarly, if silver is used as a metal substrate, then due to subsequent processing at very high temperatures, may pose recrystallization of silver as a major problem.
- Costly raw materials and poor utilization
Raw materials used in preparation of precursor salts are specialty chemicals, and as a result they are very costly. They need to be very pure and be sufficiently volatile at the MOCVD chamber conditions. Also, they need to be stable. However, some of the barium salts that are attempted are very difficult to decompose at the MOCVD chamber conditions. Also, the overall utilization of these precursor salts is low compared to the solution growth methods and as a result a significant portion of them end up on reactor walls and other undesirable places. Some solutions require use of toxic solvents such as THF (tetrahydro furan) which needs to be avoided if possible. Also, it may be difficult to maintain the proper film stoichiometry due to differences in volatility of Y, Ba, Cu-salts. Under certain conditions, some of these salts can form carbonates, and that needs to be avoided.
- Operations at very low pO_2 pressures
Deposition of HTS film and subsequent thermal treatments are carried out at very low partial pressures of O_2 as well as most likely low overall pressures to avoid adverse effects of inert carrier gas. Because of this, these complex multi-stage operations may be difficult to synchronize.
- High substrate temperature
Deposition or substrate temperature is very critical in most of the crystal growth processes and especially in MOCVD. It is found that the high J_c c-axis oriented YBCO film only grows at a narrow range of T_s , $760 \pm 10^\circ C$ by the photo-assisted MOCVD technique at a reactor pressure of 3 to 5 torr. At lower T_s , either a-axis growth or inferior crystalline quality c-axis growth would appear. On the other hand, a higher T_s would result in either a poor morphology, or the occurrence of secondary phases such as Y_2BaCuO_5 (the so-called 211 or green phase). Thus, MOCVD needs a high substrate temperature as well as precise control of it. Development of suitable non-contact heating for the required dual side deposition has been recently initiated. To achieve uniform film properties, and therefore, uniform temperature on both sides of the substrate such non-contact heating will have to be very effective.
- Need of activation or pre-buffer layer

In the past MOCVD techniques, scientists have used activation via thermal, plasma-enhanced or photo-assisted methods. Such activation is supposed to excite the molecules involved in the chemical and/or physical processes of MOCVD growth. Under infrared heating, only thermal excitations are realized and are limited by the Boltzmann distribution, whereas under photo-irradiation the full spectrum of chemical and/or physical processes can be excited through circumvention of Boltzmann distribution by photon-absorption. Similarly, the use of pre-buffer layer of Pt seems to prevent the diffusion of metal ions into the YBCO film under specific deposition conditions. All of these will make the MOCVD concept more complex and difficult to scale-up, and therefore, alternatives to them need to be identified.

- Alternative for N_2O as oxidizer
 O_2 and N_2O both are used as oxidizing gases for YBCO thin-film depositions. N_2O is known to dissociate into highly reactive species by thermal heating or other physical means of excitation. Its use as an oxidizer has led to substantial reductions in the deposition temperature of high T_c superconductivity thin films by MOCVD and PLD. However, N_2O is not stable and has an anesthetic effect, requiring careful handling and storage. The idea to add N_2O to O_2 essentially came from the consideration of the difference in ground state bond dissociation energy (for generating oxygen atoms) from these two kinds of oxygen-bearing molecular species. Whether other alternative oxidizers such as O_3 or H_2O_2 can be safely used in place of N_2O needs to be evaluated. Also the J_c plateau observed in the relationship between the J_c and $O_2/(N_2O + O_2)$ ratio needs to be explained so that possibly much higher J_c can be achieved using better oxidizer than N_2O .

Besides the above concerns, some of the other technical issues identified in the literature include:

- Difficulties experienced in reproducibly transporting the metal organics precursors to the MOCVD chamber resulting in problems with run-to-run reproducibility.
- In thick films, the quality of the film is often affected by the presence of large particles grown on the surface, affecting epitaxial structure, and consequently J_c .
- Potential of recrystallization taking place in the metal substrate core if subsequent operating temperatures are significantly higher than the substrate temperature in the MOCVD chamber. Scientists had experienced these recrystallization problems in the past when they had used silver as the substrate.
- Deposition from both sides as well as on a significantly larger surface area at acceptable rates may not be possible.
- Need fast (probably in-situ) monitoring and control systems. Also the MOCVD concept contains a large number of process control parameters, and therefore, may not be easy to control at the same time within acceptable tolerance.
- Suitable precursor salts are not yet identified and long term stability of them is questionable.

6.6 PLD Related Technical Issues

Pulsed laser deposition (PLD) is a commonly used method for growing thin films in laboratory environments where small areas of film are involved. The process is usually performed in a vacuum chamber although extremely hard vacuum conditions are not necessary and typically pressures less than 1 torr are adequate. The substrate material on which the thin film is to be deposited is mounted on a heated platen or externally heated by a lamp. The film material, termed the target, is usually positioned a few

centimeters away from and directly facing the substrate surface. A focused laser pulse is directed to a spot on the target material and a single pulse of laser energy is deposited on the illuminated spot on the target material which typically has an area of a few square millimeters. The near instantaneous energy deposition (pulse width is a few milliseconds) results in an equally near instantaneous vaporization of the illuminated target material. The vaporized target material forms a plume as it is ejected from the surface which is directed roughly normal from the target surface and normal to the substrate surface. The vaporized material plume impinges on the substrate surface and reconstitutes into a thin film of the target material on the substrate surface. An enabling characteristic of the laser induced vaporization is that since it is such a rapid process, that while plume may be comprised of electrons, ions, atoms and intermediate molecules, the stoichiometry of the target material in the plume is preserved. The substrate is heated to provide surface mobility of the impinging atoms and molecules to assist in the reconstitution of the film material. If there is a favorable lattice match of the target material and the substrate surface, epitaxial film growth on the substrate results.

While PLD is convenient for laboratory and small scale exploratory work, and even may find applications in industrial production where small area planar substrates are involved, it has several limitations in the case of producing film products such as continuous tapes. First, and probably foremost from an industrial viewpoint, is that the deposition process is quite slow. The deposition rate is of the order of an angstrom per second which means that the film thickness is an angstrom while the area may be a few square centimeters. Of course with a given laser, there are various combinations of background pressure and target/substrate separation which would possibly produce thinner films over larger areas. The point is that the laser pulse will vaporize a small amount of surface material. If the deposition rate is an angstrom per second and pulse repetition rate is 100 to 200 Hz, then it would require 50 to 100 seconds to grow a 1 micron thick film. In the case of YBCO films, a desired thickness of film to achieve reasonable engineering current densities is 10 microns which would be an order of magnitude longer.

The PLD process outlined above involves three steps: laser induced vaporization at the target surface, plume traversal from the target to the substrate, and reconstitution at the substrate surface. Let us consider each of these steps in further detail to elucidate the issues which limit the scaleup to production of thin film tapes.

The laser energy absorbed at the target surface will depend on the surface properties, the beam intensity, and the thermal diffusivity. If the optical penetration depth, that is the depth the incident radiation penetrates before it is absorbed, is less than the thermal diffusive length, the surface heating will be confined to the diffusive length. As a consequence, heat transferred to the bulk of the target material is minimized but not zero. Repeated pulsing at the same target spot would lead to thermal degradation of the target. In the case of a YBCO target, melting would result in phase impurity. A second problem is that repeated pulsing at the same location can lead to material erosion in which case sub-micron particles of the target material escape with the plume to wind up on the substrate and interrupt the orderly epitaxial film growth. To alleviate the particle problem, the target is moved between pulses or the laser beam is moved across the target. In any continuous or large area film growth, the target materials would have to have considerable ablative areas to minimize down time for changing them. While the purity of the target material has to be high, any impurities would be vaporized as well and deposit on the substrate, the utilization of the target material would be fractional due to the small depth actually used.

The plume ejected from the target surface can undergo temporal and spatial variations during its traversal from the target to the substrate. Neutral atoms and molecules in the plume will collide with each other as well as with the background gas molecules in the vacuum chamber. At 1 torr pressure with oxygen in the chamber there are still 10^{16} oxygen molecules per cm^3 . The lateral spread of the plume can be beneficial in increasing the deposition area as long as it is not accompanied by preferential molecular separation to detract from the plume stoichiometry. It is reasonable to expect that the plume diameter would double with a doubling of the target spot area which would require a four fold increase in the laser intensity.

The substrate on which the plasma impinges is heated to provide a surface mobility to the incipient molecular and atomic species of the plume. The deposition dynamics is yet more an art form for it is a combination of surface temperature, background gas pressure and plume plasma velocity which promote good film growth. On the one hand the conditions must be conducive to proper reconstitution of the species to permit epitaxial growth and on the other hand be below the threshold of sputtering the material already in place. For example, maintenance of proper surface temperature has been suggested as a potential culprit in the ability to grow good thick films of YBCO in the 2 to 10 micron range. The reasoning is that as additional depth of the film is laid down the surface temperature deviates from that of the underlying substrate material and the epitaxy becomes lost. In other words, as the film thickness increases, perhaps the substrate temperature should be increased as well.

The question as to whether one could get around the slow film growth of PLD by using an overwhelming multiplicity of PLD stations in some serial production arrangement is still open. Obviously there are some physical limitations and monetary limitations.

6.7 E-Beam Related Technical Issues

Technical issues related to the in-situ synthesization and deposition of YBCO using the e-beam co-evaporation option are concerned with proper composition, maintenance of a proper atomic oxygen environment and scale-up of the process for high rates of deposition.

YBCO is a line compound which is superconducting only with the 1-2-3 stoichiometry. In the e-beam synthesis, this means that the plume composition from the separately vaporized elemental constituents has to be carefully controlled even though different vaporization temperatures are involved. Nevertheless, according to Hammond⁽⁹⁾, some leeway in the deposited composition is afforded in the cases of Y and Cu in that these may be a few percentage points in excess of the ideal proportion without resulting in significant degradation of the critical temperature, T_c , and possibly the critical current density, J_c . However, this is not the case with barium where an excess can significantly degrade the superconducting properties. It will be extremely important to determine how closely one must approach the precise 1-2-3 composition, since more precise stoichiometry would require greater investment in sources, atomic absorption rate monitoring, and other control equipment.

Also according to Hammond's estimate⁽⁹⁾, to grow YBCO in-situ at the rate of $100 \text{ \AA/sec}$, one would require about 4×10^6 oxygen atoms per second per square centimeter. Assuming a dissociation efficiency of 20% and a large-yield scenario, his estimate calls for a flux of about 4×10^{20} oxygen atoms per second that translates into a flow of about 2220 standard cubic centimeters per minute of molecular oxygen into the atomic oxygen generator. Even though commercial equipment may be available to handle such oxygen flow rates, it needs to be demonstrated. Y and Ba deposited on the walls of the chamber will react with a significant amount of oxygen atoms, and therefore, a severe pumping requirement to maintain the low pressure (of the order of 10^{-5} mm Hg) in the chamber also needs to be demonstrated.

The e-beam co-evaporation process must be able to operate at rates approaching $\sim 100 \text{ \AA/sec}$ over multiple passes of tape, covering large areas, maintaining uniformity and running continuously for weeks at a time. Although e-beam based evaporation is utilized in other applications where continuous operation for weeks may be achieved; in situations where microscopic crystallinity is of prime importance over a large area, such a continuous operation needs to be demonstrated. On-line diagnostic and control systems for such a deposition chamber need to be developed and tested.

Finally, another important concern is identifying suitable recovery/treatment/disposal system(s) for the waste streams resulting from the process. These waste streams include the off-gases as well as collateral deposition on the walls and apparatus in the deposition chamber. For example, using BaF_2 as a source for the barium will release fluorine species in the off-gases probably necessitating corrosion resistant materials for the deposition chamber as well as any waste stream processing components.

7.0 Conclusions and Recommendations

As a result of our evaluation of the candidate options, we have reached somewhat similar conclusions that others in the field have reached in the past. The major issues for the economical manufacturing of the long-length YBCO-coated conductors pertain to capability of uniform depositing at high rates over a large area with continuous process times. Of course such capability has to meet the other important requirements of proper stoichiometric composition and epitaxial crystalline structure.

From our current evaluation, we have identified MOD, Sol-Gel, MOCVD, E-Beam and PLD as leading candidates from two different types of deposition techniques. But the other options can be equally good or bad in manufacturing the different substrate shapes and for different applications. As more work is done on different options, additional information will become available and as a result it is possible that the preliminary rankings developed at present based on different emphasis areas may change.

For the selected candidates, various technical issues are discussed earlier, however, categorically they all fall into the following generic areas where additional research and development work is recommended/needed.

- Cost of chemicals--

Need to find cheaper salts or develop alternate but simple ways of making them.

- Mass transfer and reaction kinetics data--

To design a deposition chamber, pyrolyzer or thermal treatment (oxidizer, cooler, etc.) rates at which the chemical transformations are taking place and/or the species are being transported across the phase boundaries need to be known. Appropriate mathematical models need to be developed from the laboratory scale experience so that the data/results can be scaled-up to larger/commercial scale systems.

- Diagnostics and control--

Requirement of a high J_c performance necessitates very sophisticated and quick response type diagnostics and control system. On-line control systems to meet such needs are either not sufficiently developed or do not exist. Experiences from the related commercial operations can be useful, but the needs may be quite different; and therefore, parameters of importance and ways and means to monitor them on-line may need significant efforts.

- Environmental issues--

Even though the quantities of chemicals used and waste products (liquids and gases) produced will be small in comparison to other manufacturing industries, with the ever increasing demands on the environmental acceptability and compliance, the major waste products from the system will need to be identified, characterized and then appropriate recovery/treatment/disposal options need to be developed.

- Outer passivation/insulation layer--

No work has been reported that deals with the outside passivation/insulation layer. With YBCO being chemically sensitive to moisture and air, an effort needs to be started to identify suitable candidates for this protective layer as well as the appropriate method to apply them over the coated conductor wires/tapes.

- Splice connections--

It seems that in commercial manufacturing of long-length coated conductors, a significant fraction of the production may not meet the product specifications. As a result, need may exist to connect sections of the good/acceptable wires to make a long wire of desired length for economic reasons. To maintain continuity in the superconducting properties at such connections, suitable material as well as appropriate technique to incorporate them will be needed.

- Corrosion, toxicity, health hazards, etc.--

So far, in the laboratory scale/experiments, these factors are usually given less consideration, but for the future commercial systems they will have to be given proper attention otherwise the cost of producing long-length conductors can escalate significantly.

- Overall cost of production--

Because all the sequential steps in the processing of a coated conductor wire are not carried out yet, the estimated cost of production has become a kind of a number game in which attempts have been made to come up with the target/desired overall cost figure without providing adequate details or justifications for the various cost parameters that are involved in its development. An unbiased effort needs to be made with the help from the industrial partners to develop cost of the finished product using available information and standard estimating procedures. If the final number comes close to the desired target then it is fine otherwise at least such an effort will identify the areas where the costs need to be reduced.

In general, our evaluation has identified a serious need for addressing the coated conductor wire program from the perspectives of engineers. The science and chemistry developed so far or being developed in isolated islands type situations now need proper engineering assistance/viewpoints so that an overall objective of developing a viable commercial process does not get lost!

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