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TOPICAL REPORT

EVALUATION OF METHODS FOR APPLICATION OF EPITAXIAL LAYERS OF SUPERCONDUCTOR AND BUFFER LAYERS

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1.0 Executive Summary

The recent achievements in a number of laboratories of critical currents in excess of $1.0x10^6$ amp/cm^2 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-axial texturized 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 Protective 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. It also provides the approach being used to develop the cost information as well as the major operational parameters/variables that will have to be monitored and the relevant control systems. 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 (MOD), Sol-Gel, and E-Beam as the Leading Candidates, and Technical Concerns/Issues that Need to be Resolved to Develop a Commercially Viable Option Out of Each of Them.
- Process Control Needs for Various Schemes
- Approach/Methodology for Developing Cost of Coated Conductors

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 the different materials. 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 $1.0\text{x}10^6$ amps/cm^2 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 intergranular critical current density approaches the film intragranular 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 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 scaleable to a commercial scale without incurring developmental studies and costs which are not considered herein.

3.0 Description of Typical HTSC Wire/Tape Manufacturing System

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 $YBa_2Cu_3O_{7-\delta}$ (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 ≥900°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.

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(1):

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

- 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.(1)

- 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:(1)

- Chemical Vapor Deposition (CVD) Techniques
    - + Metallo-organic Chemical Vapor Deposition (MOCVD)
    - + Plasma or Photo-Assisted MOCVD
- Sol-Gel (Spin/Dip-Coating, Spraying, Painting)
- Metal-Organic 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(2), 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 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 protective 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, substrate, buffer, HTS and outer protective layer. From our literature search no information was found about any work that has taken the concept from the substrate at one end and produced a finished 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

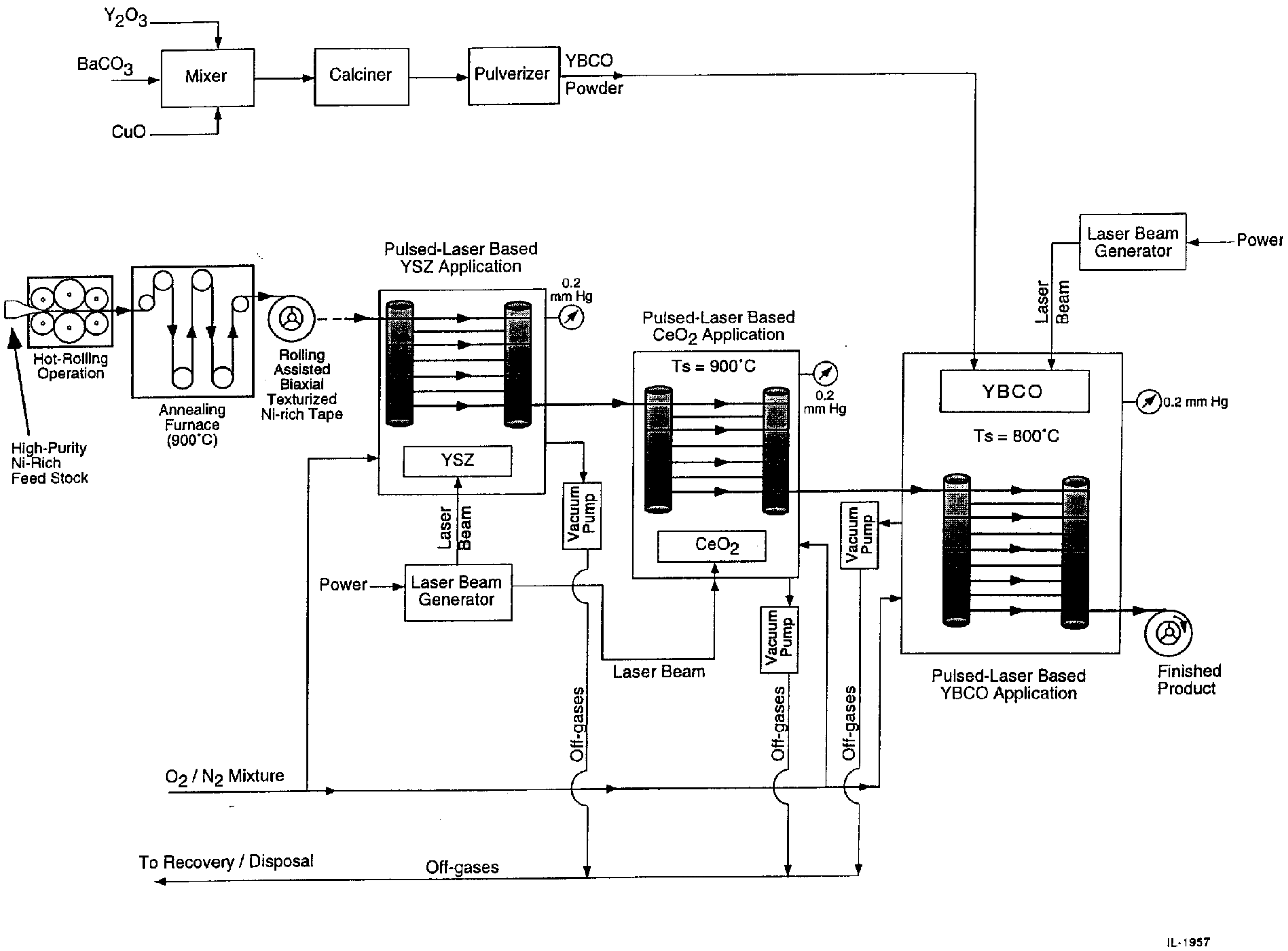
In the schematics for various options, we have also included two leading concepts; IBAD and RABiTS for preparing a textured crystalline substrate or substrate-plus-buffer composite. The necessity of having a suitably textured/crystalline substrate over which the layers of buffer material and then the HTS film can be grown in an epitaxial manner has been very strongly emphasized. It has been claimed that unless one starts with a suitably textured/crystalline substrate or substrate-plus-buffer composite, the high J_c values expected from the finished product will not materialize.

The process schematics for each of the candidate options listed above, and also incorporating the IBAD or RABiTS technique for texturization are shown in Figures 1-9. The brief descriptions on each of these flow sheets are as follows:

3.1 Pulse Laser Deposition/Ablation

Process schematic incorporating RABiTS-based substrate texturizing options with the pulse laser-based buffer materials and YBCO depositions are shown in Figure 1. The major operating steps involved in this scheme are:

- preparing a texturized Ni-rich alloy tape using the RABiTS-scheme.
    - In the RABiTS scheme, a block material of Ni-rich alloy/feed stock is hot-rolled into a tape form of required thickness.
    - The rolled tape is then annealed at about 900°C for a few hours to relieve stresses
    - The stress-relieved tape is wound on a spool and transported to another site where applications of the buffer material(s) and YBCO are carried out--or if it is carried out at the same site then introduced to that part of the processing without going through a spool in a continuous mode of feeding.
    - Under the desired level of O_2 in N_2, the texturized tape is deposited with the YSZ material at low pressure. The vaporization of YSZ from the source and deposition on the tape at desired rate are controlled by the laser based deposition system.
    - Off-gases from the chamber where YSZ is being deposited are collected and taken for recovery or disposal.
    - Next, the YSZ layered tape is further deposited at high temperature (~900°C) with CeO_2 using the identical technique as the YSZ deposition.



CONDUCTOR COATING SCHEME FOLLOWING PLD METHOD

FIGURE 1

- Off-gases from CeO_2 application chamber are also led to the recovery or disposal section.
- 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 to the necessary particle size.
- Ground YBCO powder is then used in forming the YBCO film over the CeO_2/YSZ/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 also 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 protective/insulative layer would be formed before winding the finished tape on the spool.

According to recent information from the Oak Ridge National Laboratory (ORNL)[3], on the RABiTS-based texturized 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 $1X10^6$ A/cm^2 at 75K. If this ORNL result is consistently confirmed in the future then the scheme shown in Figure 1 will be simplified by eliminating the need for the YSZ layer deposition on the RABiTS-texturized Ni-rich alloy substrate. For our present evaluation, However, we have included the original two buffer layer schemes for further analysis.

3.2 E-Beam Based Deposition

Process schematic incorporating Ion-Beam Assisted Deposition (IBAD) of YSZ and YBCO deposition by E-beam technique is shown in Figure 2(21). Unlike RABiTS, the IBAD technique develops texturized film of YSZ on the Hastelloy or Ni-rich tape, by properly orienting the angle of the electron beam with the aid of Argon ions with respect to the substrate surface. Thus, mechanical rolling and subsequent annealing necessary in case of RABiTS are not required to develop the texturized substrate. It is also not known whether the initially texturized Ni-rich alloy tape if deposited with YSZ using IBAD based E-beam technique would give a better product or not. The major steps involved in the IBAD/E-Beam based deposition of YSZ and YBCO on suitable substrate are as follows:

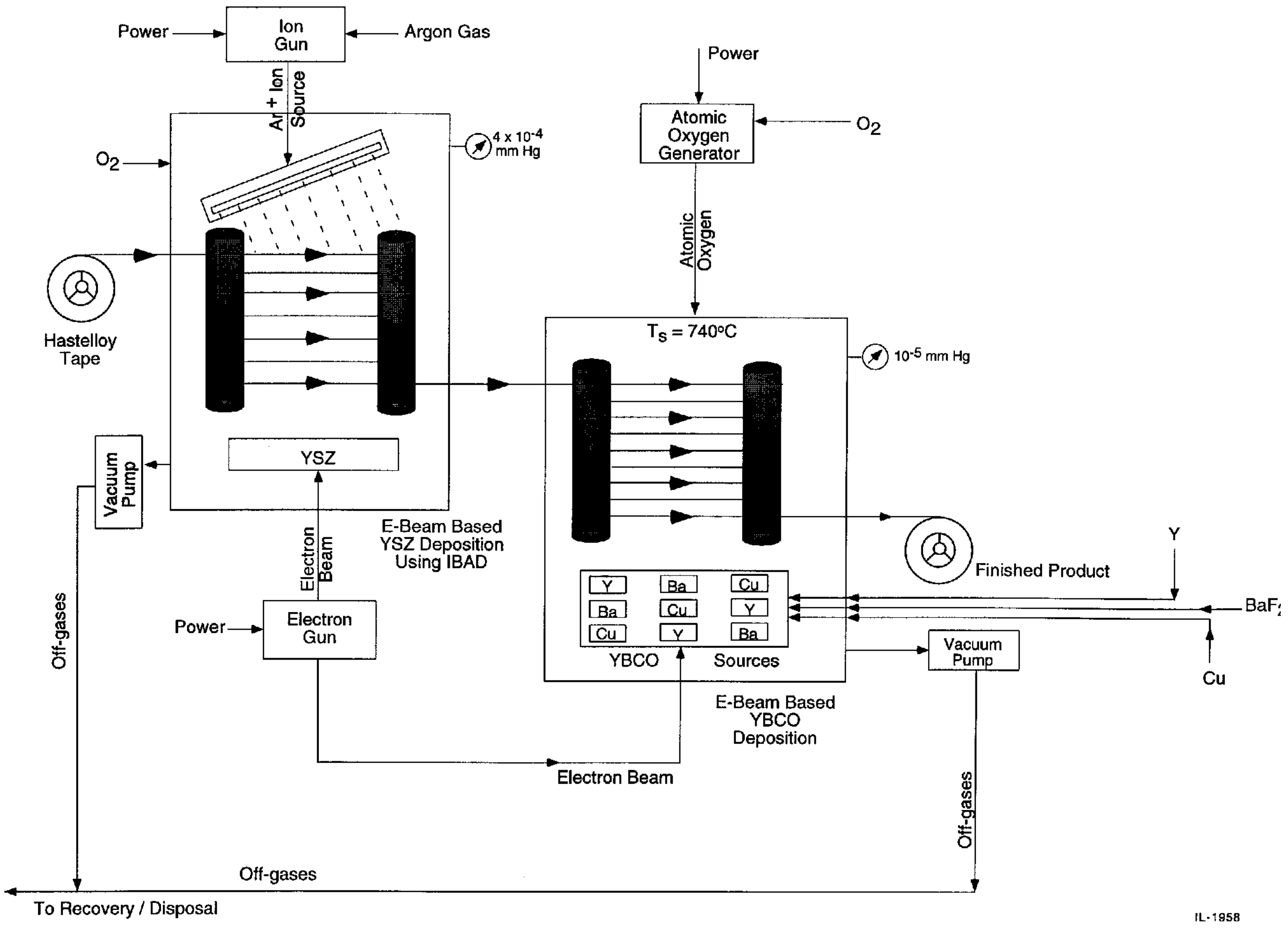
- Hastelloy or Ni-rich alloy tape in required dimensions is continuously fed to the chamber where YSZ layer is deposited using the IBAD/E-beam technique. Argon ion beam is provided by the ion gun that ionizes the argon gas. The electron gun provides the electron beam necessary to energize and vaporize YSZ from the container maintained in the chamber. Pressure in the chamber is maintained at a very low level.

- Off-gases from the above chamber are collected and sent for recovery or disposal.

- YSZ layered tape then enters the next chamber where 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. 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 protective/insulating layer or technique to apply are not yet



E-BEAM BASED CONDUCTOR COATING METHOD UTILIZING IBAD TECHNIQUE FOR BUFFER APPLICATION

FIGURE 2

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 apriori and then deposited on the texturized 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 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 an oxide form, and therefore, 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.

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. Combining the steps of RABiTS and MOCVD, the simplified process schematic to produce YBCO-coated conductor will be as shown in Figure 3. Again, all the steps are not shown here and even the ones shown here are not 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

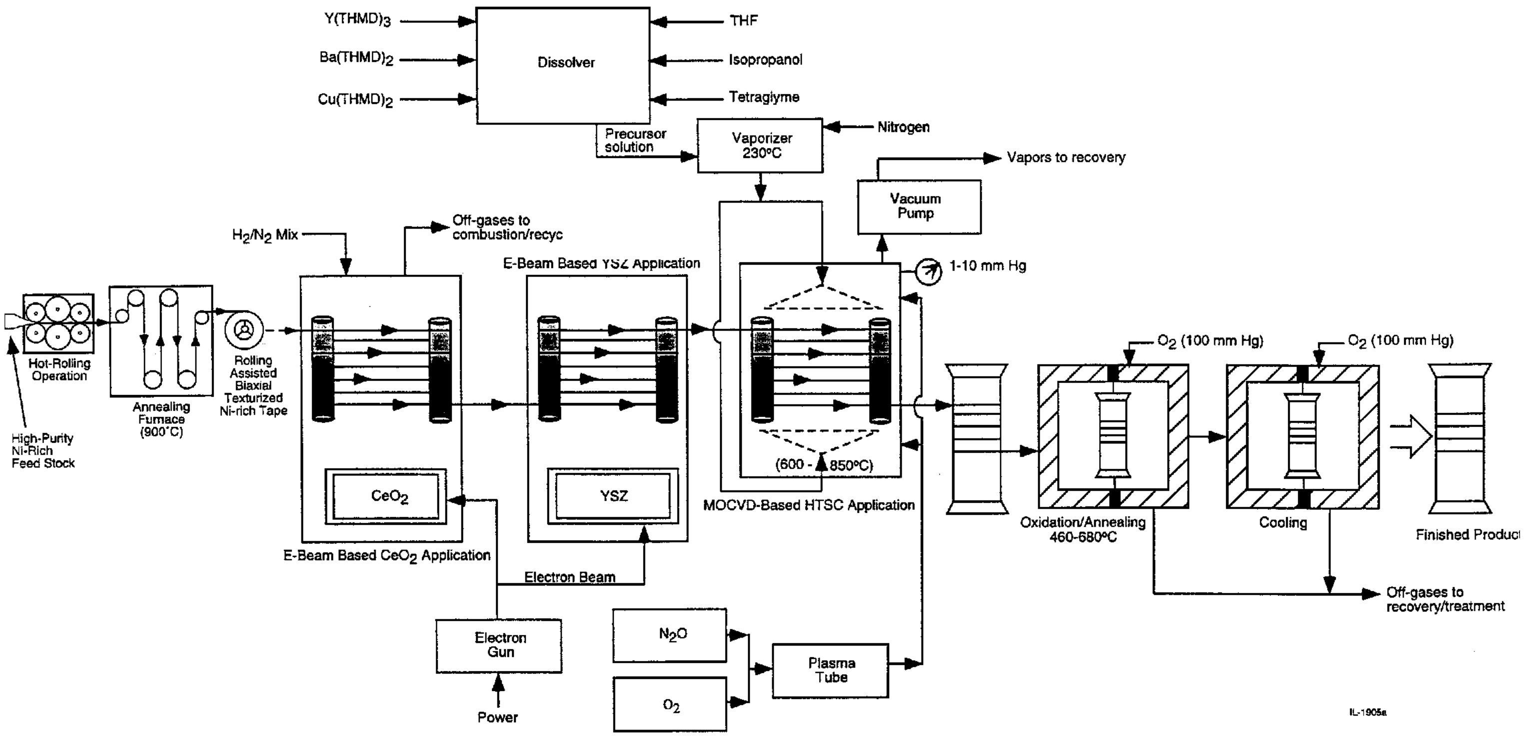
This step usually would be carried out off-site by some chemicals manufacturing company and the conductor coating company would probably buy the solution mixture from them. It is anticipated that a mixture of $Y(THMD)_3$, $Ba(THMD)_2$ and $Cu(THMD)_2$ (where THMD stands for 2,2,6,6-tetramethyl -3-5 Heptanedionate 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.

- Substrate is usually a nickel-rich alloy which is prepared in a desired form (width, thickness and texture) by undergoing the RABitS treatment described earlier. Again this substrate preparation can be carried out on-site or can be carried out off-site and delivered to the site where the conductor and buffer coatings are carried out on a spool.

- Texturized nickel-rich alloy tape is then continuously introduced into a chamber where CeO_2 layer is applied using the E-beam deposition technique. To prevent the possible oxidation of nickel, a reducing atmosphere consisting of H_2 and N_2 needs to be maintained.

- Off-gases from this chamber would be collected and either incinerated (due to unreacted H_2) or recycled after necessary cleanup.

- Tape coming from CeO_2 application would then go to another chamber where YSZ layer would be applied using the E-beam deposition technique. As said earlier, in a recent ORNL news(3), the need for this YSZ layer is described to be not necessary. However, it is not clear whether it is not necessary when the YSZ layer is laid first and then CeO_2 is applied or vice versa.



CONDUCTOR COATING SCHEME FOLLOWING MOCVD METHOD

FIGURE 3

For the time being, based on the available older literature, we have kept both the buffer application steps in our scheme.

- Off-gases from the YSZ application chamber would be led to recovery/disposal section.

- YSZ/CeO_2/Ni-rich texturized tape then 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 N_2O/O_2 plasma is introduced from the plasma generator tube and vapors of Y,- Ba, - Cu,- precursors are brought in by flowing N_2 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 texturized crystalline structure of the resulting HTS film.

- In the oxidation/annealing and cooling chambers the partial pressure of O_2 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 protective/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.

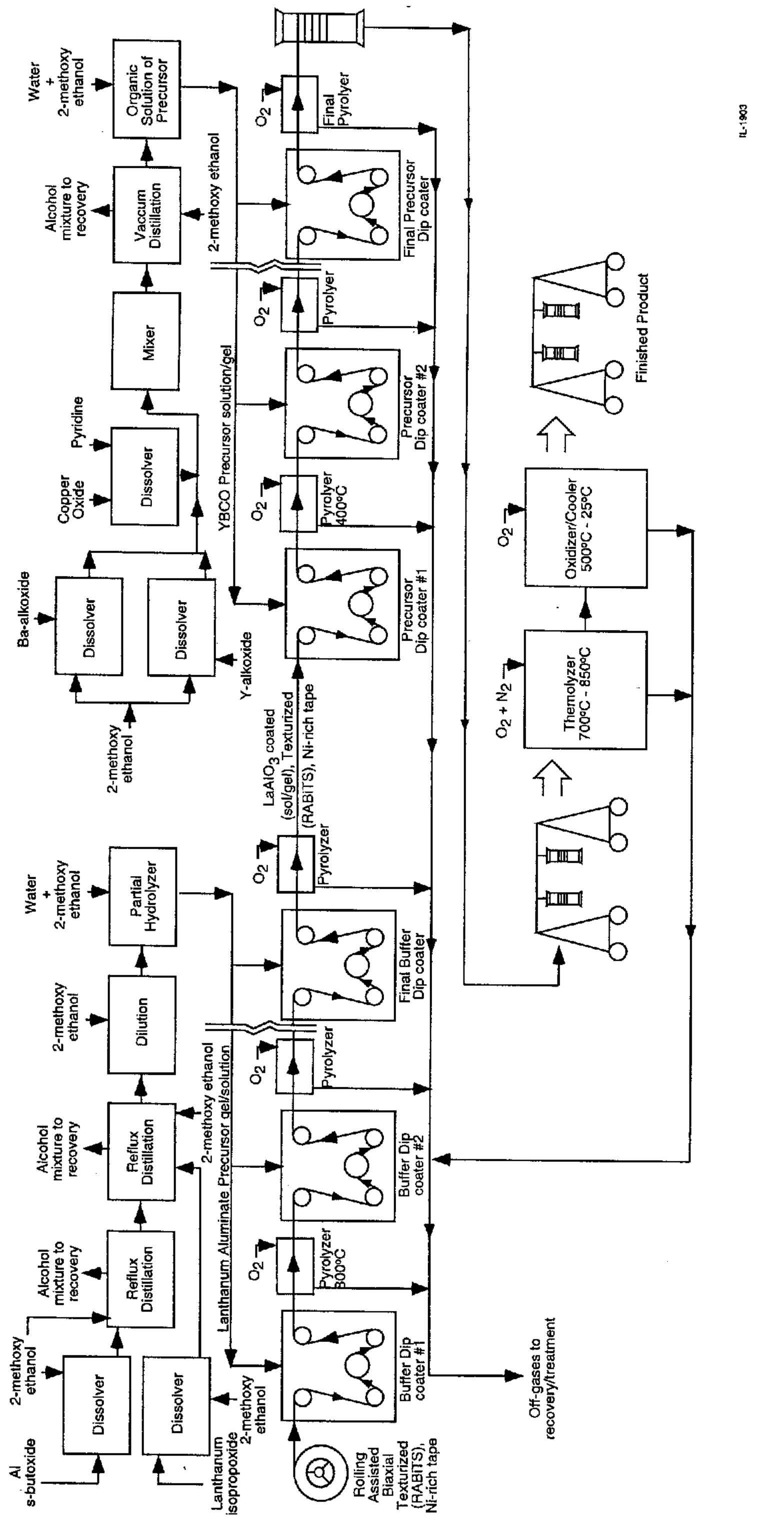
3.4 Sol-Gel Method

This option is based on the solution growth technique and does not use any high energy particles (ions, electrons, photons, etc.) for transportation, vaporization and coating of 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 layer of suitable buffer layer (e.g. $LaAlO_3$) by this technique as well as forming a superconductor layer (e.g. YBCO) by this sol-gel technique is shown in Figure 4. In reality it should be possible to coat the HTS layer by a sol-gel technique on a substrate/buffer composite that was previously prepared with coating of YSZ or some suitable buffer material using any other physical/non-physical technique. The major steps involved in the proposed scheme are as follows:

- Preparation of gel/solution containing $LaAlO_3$ precursor

Such a gel/solution in commercial preparation of a gel/solution containing $LaAlO_3$ precursor practice would be available from a supplier of specialty chemicals. But for the sake of completeness it is assumed that it is produced on site. In that case the steps involved in its preparation would be as follows(4).

  - solution of aluminum s-butoxide and lanthanum iso-propoxide in 2-methoxy ethanol undergo reflux distillation and then partial hydrolysis to convert organic solution mixture to gel/solution of required concentration and flow characteristics. This precursor



CONDUCTOR COATING SCHEME FOLLOWING SOL-GEL METHOD

Figure 4

gel/solution is then used to coat a suitable substrate. Alcohol vapors coming out of the distillation step during such processing would need some kind of recovery/disposal operation.

- It is assumed that a texturized substrate (Ni-rich alloy tape) is available for coating the buffer solution. In the scheme here it is shown that such a material texturized by the RABiTS technique (see Figure 1 or 3) is either produced on-site or off-site and is available on a spool.

- Texturized Ni-rich tape is pulled through a chamber which is filled with the precursor gel/solution of lanthanum aluminate. Since it is expected that the desired overall thickness cannot be achieved in one such chamber, a multi-stage coating operation is shown here. In between each state, a pyrolyzer is needed to convert the precursor film to lanthanum aluminate by vaporizing the organic solvent and oxidizing. It is believed that crystallization of the deposited buffer material on the texturized substrate also takes place during this pyrolysis. After going through a number of such coating chambers and pyrolyzers in series, the composite of the buffer and Ni-rich tape will be ready for the HTS coating.

- 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.

- Preparation of gel/solution containing precursor for YBCO.

    - Again, this 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(5), 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 buffer coated Ni-rich alloy tape is now coated with the YBCO precursor gel/solution. Again 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 400°C to vaporize organic solvent and to oxidize. By doing so in small steps, it is believed that some or total crystallization of the YBCO phase also takes place during this operation in an epitaxial manner with the already deposited/texturized YBCO and buffer layers.

- Similar to coating operations for the buffer coating, YBCO application phase would also need recirculation and recovery/disposal sections for circulating YBCO precursor gel/solution and for treatment of off-gases from pyrolyzer, respectively.

- The HTS-coated buffer/Ni-rich alloy 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 700-850°C followed by progressive cooling in an oxidizing atmosphere to room temperature.

- Before sending out to customer, the HTS-coated tape will be coated with some kind of protective/insulating 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 buffer coated, texturized Ni-rich alloy tape is shown in Figure 5. It is assumed here that this YBCO coating technique would work on any substrate. As a result, even though in this particular scheme it is assumed that the buffer layer of $LaAlO_3$ is applied by the sol-gel method to texturized (by RABiTS technique) Ni-rich alloy tape; in commercial practice substrate prepared by other techniques can also be used. The part of the flow sheet that would correspond to the application of $LaAlO_3$ by the sol-gel technique to the texturized Ni-rich alloy tape would be the same as shown in Figure 4, and therefore, it is not repeated here in the Figure 5. The major operations involved in the scheme shown in Figure 5 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(6) temperatures for vaporization are maintained at 820°C for YCl_3, 950°C for BaI_2 and 340°C for CuCl.

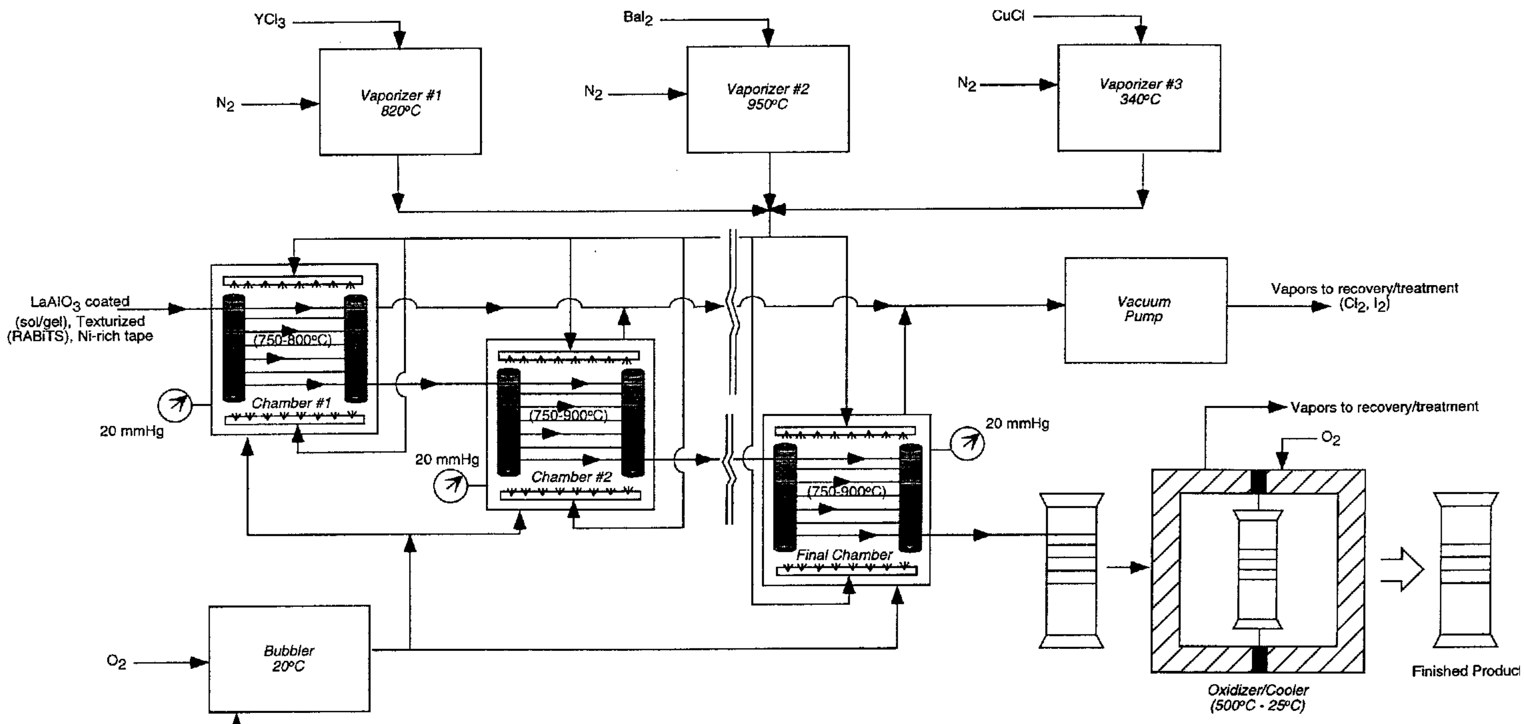
- It is assumed that on a continuous mode a $LaAlO_3$ layered, texturized Ni-rich tape is available for chemical coating by the above vapor mix.

- The buffer coated 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 gas as the carrier gas. In each chamber moist O_2 will also be introduced and the chamber temperature of 750-800°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 form and in 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 protective/insulating



CONDUCTOR COATING SCHEME FOLLOWING CVD METHOD

FIGURE 5

layer, but its type as well as method of application are not yet determined. As a result, this is not shown in Figure 5.

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 buffer coated Ni-rich tape that is properly texturized 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 6. In this scheme we have assumed that a Ni-rich alloy tape can be texturized (as discussed before) by a RABiTS technique and then coated with the $LaAlO_3$ buffer using the sol-gel technique (also discussed before). In the commercial application, aerosol spraying and subsequent pyrolysis should work on a substrate prepared by other techniques also. The major operations involved in the scheme shown in Figure 6 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(7,8). This aqueous solution of nitrates is then atomized in various spray chambers to provide the coating of nitrate precursor on a suitable substrate.

- It is assumed that on a continuous mode, a $LaAlO_3$ coated, texturized Ni-rich alloy tape is available for chemical coating by the above solution of nitrates.

- The buffer material coated 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.

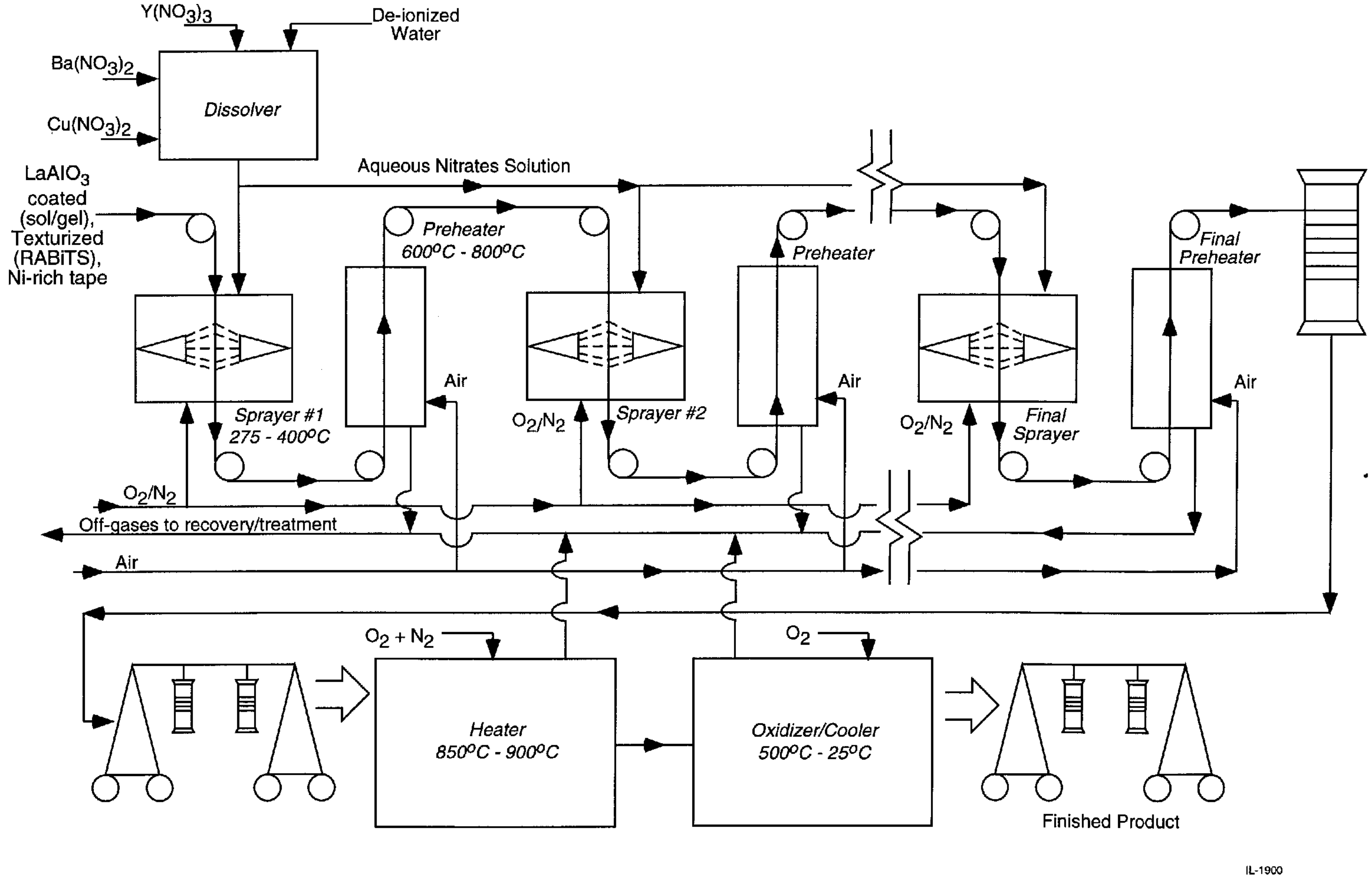
- This spraying of nitrate aerosol and preheating/decomposition is continued in a number of stages in a series till overall thickness of the YBCO layer as well as epitaxial texture of the composite are achieved.

- 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 800-900°C under proper O_2 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



CONDUCTOR COATING SCHEME FOLLOWING AEROSOL/SPRAY PYROLYSIS METHOD

FIGURE 6

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 protective/insulating 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.

- 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 is carried out on $LaAlO_3$ coated texturized Ni-rich alloy tape. The texturization of Ni-rich tape is assumed to be carried out by the RABiTS technique and the deposition of $LaAlO_3$ on Ni-rich alloy tape is assumed to be carried out by the sol-gel option described earlier. In a commercial process, these two steps can be carried out by other suitable options. The process scheme employing metal organics decomposition (MOD) option is shown in Figure 7. The major operations involved in this scheme are as follows:

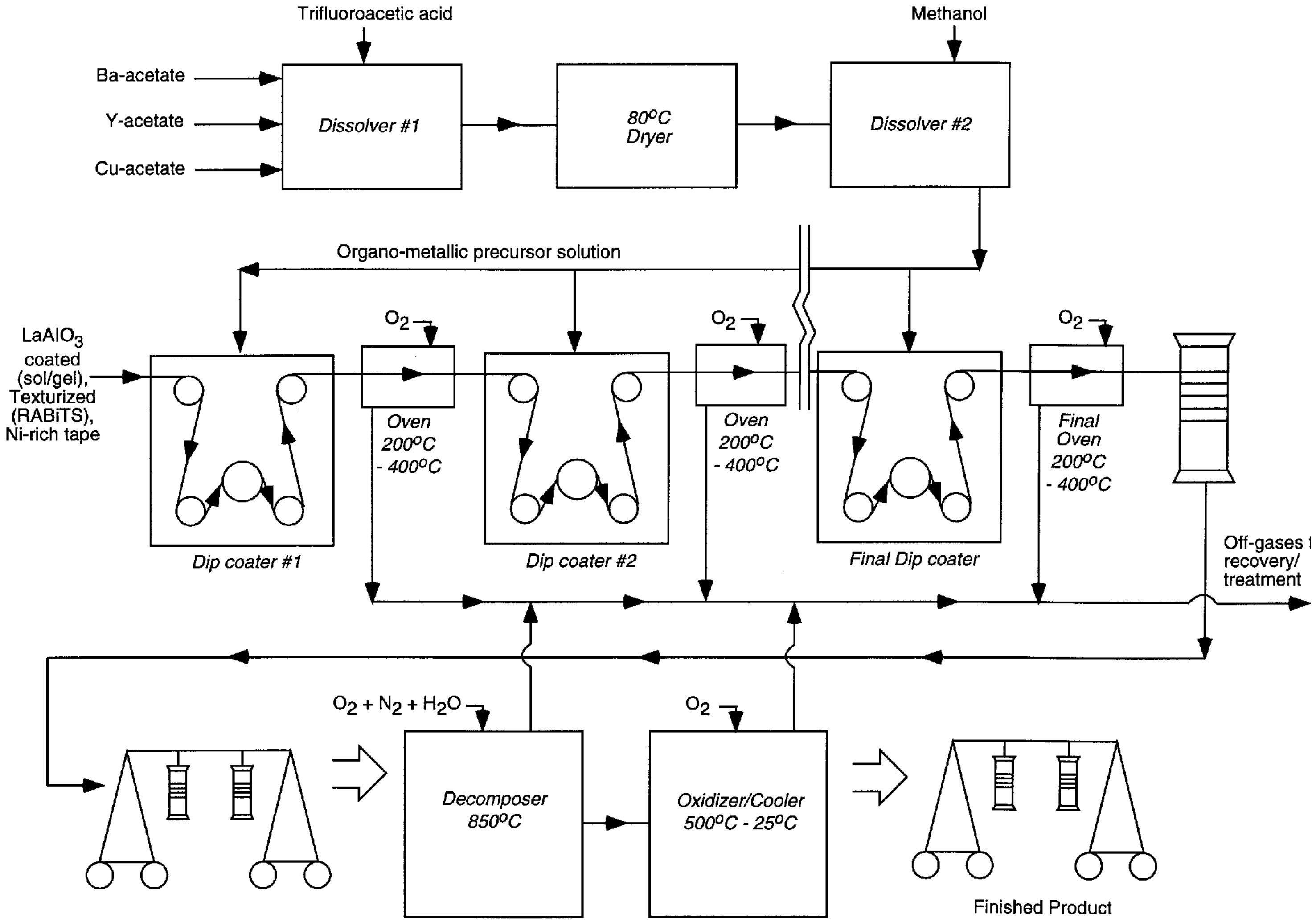
- Preparation of precursor salts solution.

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(9). 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.

- It is assumed that on a continuous mode, a $LaAlO_3$ coated, texturized Ni-rich alloy tape is available for dip coating of the trifluoroacetate solution.

- The buffer material coated 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.

- The coated tape then enters the oven maintained at about 200-400°C under O_2 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 a number of such sequences are carried out in a series type of operations to achieve the desired overall thickness. In a commercial



CONDUCTOR COATING SCHEME FOLLOWING MOD METHOD

IL-1902

FIGURE 7

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 oven 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 N_2/O_2 atmosphere where oxyfluoride form of the precursor gets converted to the oxide form and the crystallization is also completed.

- In the second stage the tape undergoes cooling at a controlled rate in the O_2 atmosphere.

- Off-gases from both these stages will need some kind of recovery/treatment operations prior to disposal.

- Similarly, the HTS coated tape would then be further coated with some kind of protective/insulating layer. Details about these are not available at present.

3.8 Electrodeposition

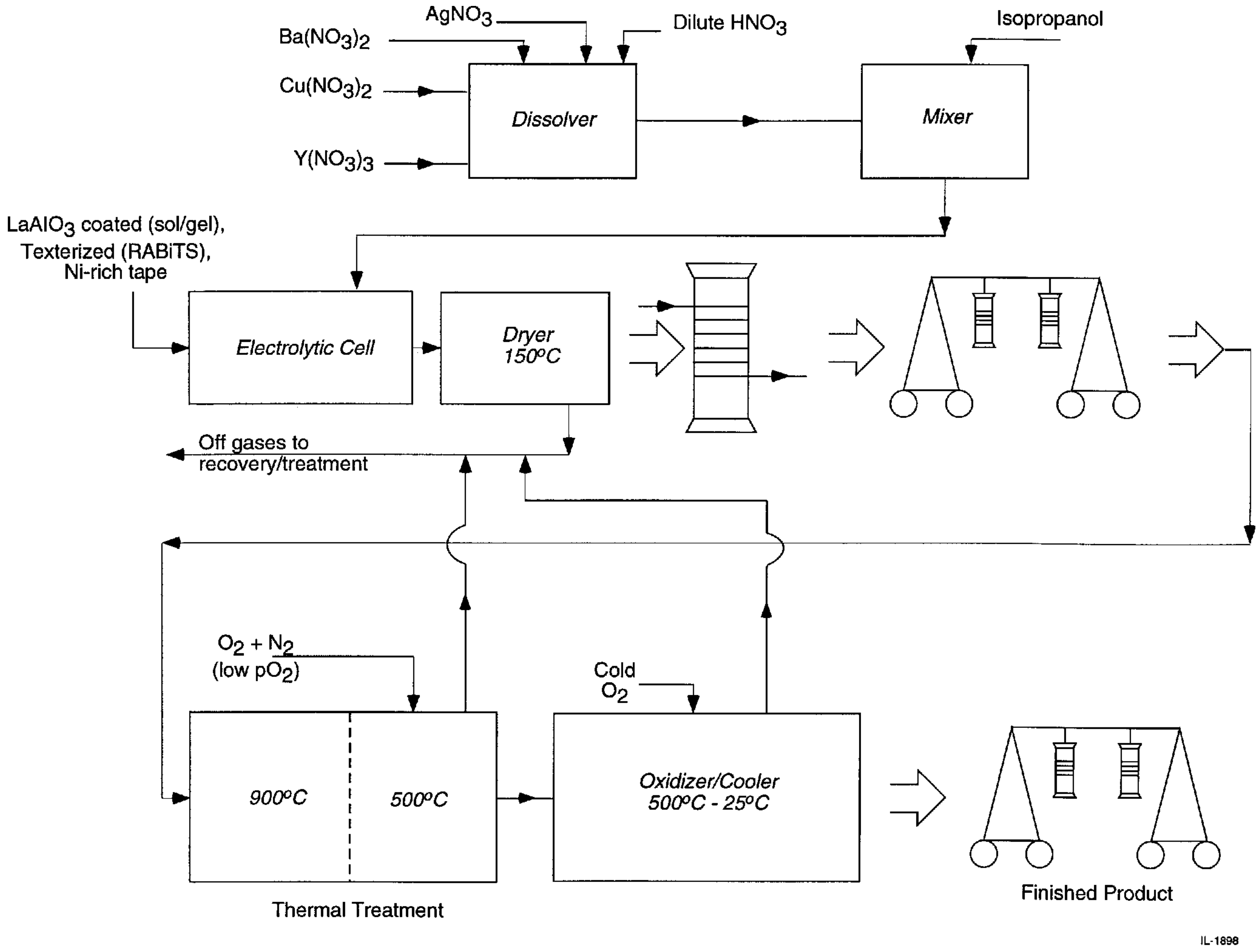
This is an electrochemical method whereby dissolved material in an ionized form is uniformly deposited over the substrate maintained at the appropriate polarity. In the literature, no information was found for applying buffer coating over the metal substrate, and therefore, it is assumed that a buffer coated suitable substrate will need to be prepared by some other method. A process schematic incorporating this electrodeposition method for a buffer-coated Ni-rich alloy tape is shown in Figure 8. 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(10). But later on to avoid possible incorporation of sulfur from DMSO in the HTS film, Abolmaali and Talbot replaced DMSO with Isopropanol(11). 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, $Ba(NO_3)_2$, $Cu(NO_3)_2 \, 2{\cdot}5 \, H_2O$, and $Y(NO_3)_3{\cdot}6 \, H_2O$). Initially, the nitrate salts are dissolved in an acidified (with dilute HNO_3 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.

- It is assumed that on a continuous mode, a $LaAl0_3$ coated, texturized Ni-rich alloy tape is available for electrochemical deposition of the nitrates precursor solution.

- The buffer material coated 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 a recirculation system so that buildup of undesirable species in the electrolyte can be controlled at



CONDUCTOR COATING SCHEME FOLLOWING ELECTRODEPOSITION METHOD

FIGURE 8

or below the acceptable level by taking a slip stream. This slip stream will need to be appropriately 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. $Cu(OH)_2$ and some $Y(OH)_3$ start decomposing to the respective oxide forms. For $Ba(OH)_2$ the decomposition to oxide form needs a higher temperature (about ≥ 560°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 pO_2) atmosphere. Required epitaxial structure 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.

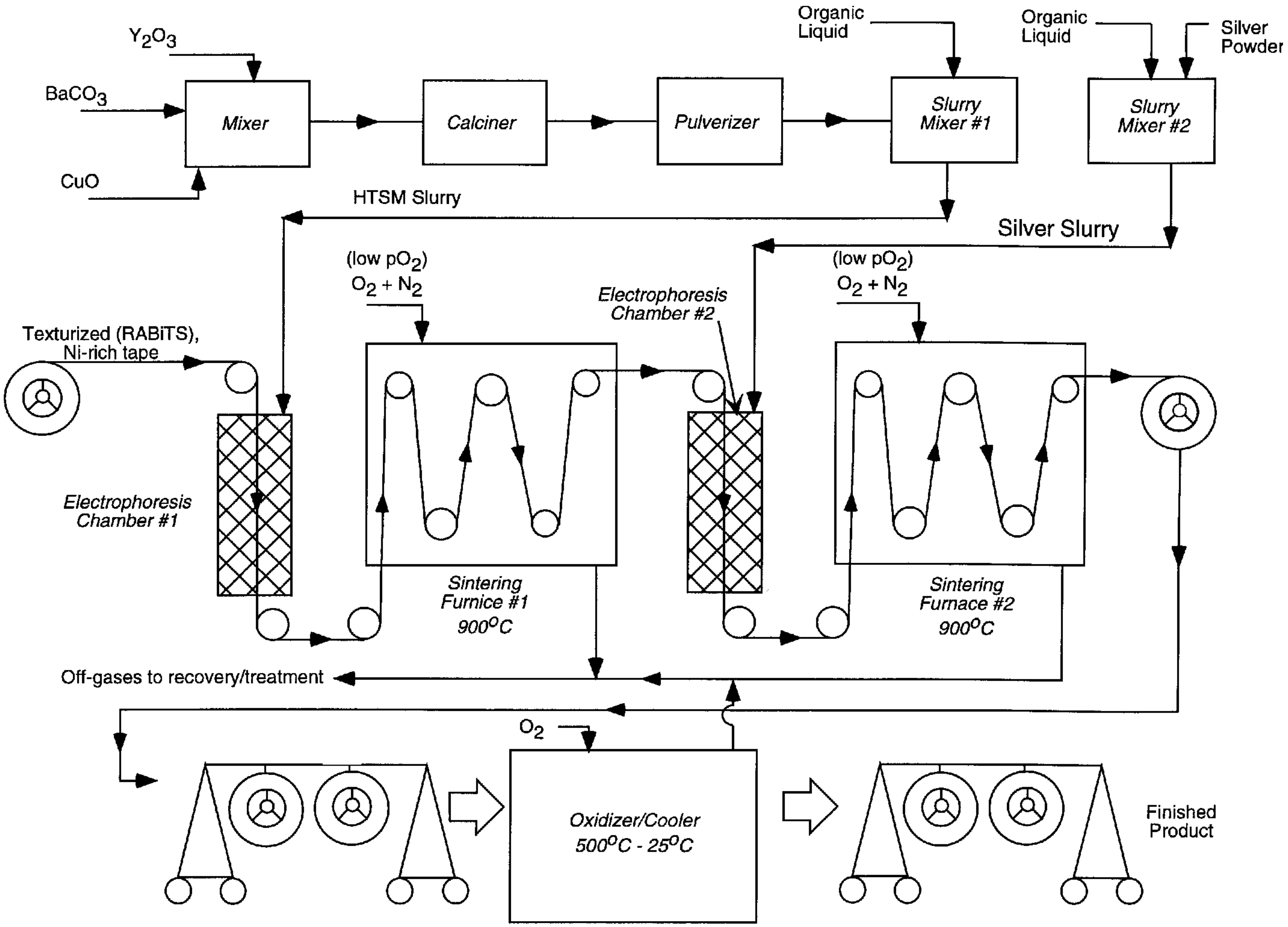
- Off-gases from both phases of the thermal treatment will be collected and treated appropriately prior to disposal or recycle.

- The cooled spools can either go to the stage where outer protective/insulating 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(11), 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 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)(2). However, they did not start with the texturized metal substrate wire, 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-texturized wire. This slightly modified version of their processing scheme is shown here in Figure 9. The major operating steps involved in this scheme are as follows:

- Preparation of YBCO (HTSM) slurry
  - Superconducting powder material of composition $YBa_2Cu_3O_{7-x}$ 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 0.5-10µ and then suspended in a non-aqueous liquid. General Atomics'



CONDUCTOR COATING SCHEME FOLLOWING ELECTROPHORESIS METHOD

IL-1899

FIGURE 9

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.

- It is assumed that the texturized Ni-rich alloy tape is available on a spool form or can be prepared using the RABiTS technique as shown in Figure 1. It is also believed that a layer of buffer material is not required so the YBCO (HTSM) coating is applied right over the texturized metal substrate tape.

- In the electrophoresis chamber #1, the texturized Ni-rich alloy tape is continuously fed. The YBCO slurry contained in this chamber under electrophoretic forces forms a coating on the continuously vertically moving wire. By adjusting the speed of the wire 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 passed into the sintering furnace #1 which is maintained at 900-1030°C under O_2/N_2 (low pO_2) atmosphere. According to the GA information, about 1 to 30 minutes are 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(2) 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 O_2 atmosphere at about 850-950°C. The residence time required ranges based on the GA work, from 0·2 to 10 minutes. Off-gases from this sintering furnace is also led to the recovery/treatment section where it is 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 wire/tape are further oxidized in a chamber where O_2 atmosphere is maintained and temperature is kept around 400-500°C. According to the GA literature(2) 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 wire/tape that comes out of the above scheme would need additional layers of outer coating/insulation 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. 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.

4.0 Process Evaluation

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(1) and Julia Phillips at Bell Lab(13) have attempted such evaluations on a limited scope. Julia Phillips concentrated her review mainly about selecting the suitable substrate for subsequent deposition of high-temperature superconducting thin films. For substrate selection, she considered the following criteria as important areas:

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

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

Paranthaman's(1) 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 this 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-Organic and Chemical Vapor Deposition
    - Sol-Gel
    - Metal Organic 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, he 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 quantative data for only a very few parameters were available. Hence, it was decided to use the available quantative 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(14). 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, ----x_n) can be expressed as:

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

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

SUBSTRATE		BUFFER		SUPERCONDUCTOR		OUTSIDE COVERING	
Materials Related	Pretreatment Releated	Materials Related	Application Process Related	Materials Related	Application Process Related	Materials Related	Application Process Related
Chemistry & Materials Related Parameters:							
Compatibility	Rolling Characteristics	Compatibility	Smoothness	Compatibility	Film Surface Quality	Compatibility	Smoothness
Mechanical Properties	Texture/ Orientation	Availability	Continuous/ Semi-Continuous	Precursor Availability	Large-Area Coverage	Availability	Continuous/ Semi-Continuous
Availability	Annealing	Thermal Expansion	Biaxially Aligned	Chemical Stability	Deposition Rate	Mechanical Properties	Coating Thickness
Cost	Surface Roughness	Chemical Stability	Deposition Rate	Cost	Coating Thickness	Cost	Reduction in J_c
Thermal Expansion	Grain Boundary Characteristics	Latice Mismatch	Coating Thickness	Thermal Expansion	Continuous/ Semi-Continuous	Thermal Expansion	
		Need for Multi-Layers	Material Utilization	Latice Mismatch	Flim Stoichiometry	Oxidation Resistance	
		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					
Engineering & Environmental Based Process Parameters:							
	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		

Table 1

where:

w_i = weight (scaling) factor for ith attribute, and

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

A utility function $U_i(x_i)$ was specified such that for each attribute x_i, $U_i\left(x_i = x_i^l\right) = 0$ and

$U_i\left(x_i = x_i^h\right) = 1.0$. In other words, the worst outcome $\left(x_i = x_i^l\right)$ for each attribute was assigned a utility of zero and the best outcome $\left(x_i = x_i^h\right)$ was assigned a utility of 1.0. 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:

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

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:

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

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(15,16). 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 quantative information were available in the literature;

- Process Severity (Temperature and Pressure)
- Thermal Expansion Coefficient Mismatch
- Lattice Parameter Mismatch
- Coating Thickness for Buffer and HTS Material
- Deposition Rate for Buffer and 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 Thermal Expansion Coefficient Mismatch

The thermal expansion coefficient mismatch between the substrate and the buffer layer and between the buffer layer and the superconductor layer can cause uneven expansion or contraction of the layers resulting in thermal stresses in the coated conductor. Such a stress is usually related to the difference between the thermal expansion coefficient of the individual layers. The following approach was used in calculating the attribute/merit for the candidate options based on the thermal expansion coefficient mismatch parameter.

- DATA USED:

Substrate	***Thermal Expansion Coefficient*** $\propto x10^6\ k^{-1}$	***Reference No.***
Hastelloy	11.2	17
Ni	13.3	18
Ag	19.68	19
Buffer		
CeO_2	9	1
YSZ	10	20
MgO	13.8	20
$LaAlO_3$	10	20
$SrTiO_3$	10.8	20
Superconductor		
YBCO	12	1

- Assumption Made: The analysis is assumed to be done at 200K (the lowest reported temperature).

- Definitions of the equations used for comparison:

$$\Delta \propto_i = \left| \propto_{HTSC} - \propto_{buffer\ 2} \right| + \left| \propto_{buffer\ 2} - \propto_{buffer\ 1} \right|$$
$$+ \left| \propto_{buffer\ 1} - \propto_{substrate} \right| \text{... for two buffer layers}$$

$$\Delta \propto_i = \left| \propto_{HTSC} - \propto_{buffer\ 1} \right| + \left| \propto_{buffer\ 1} - \propto_{substrate} \right| \text{... for one buffer layer}$$

$$U_i = \sqrt{1 - X_i^2} \ \text{ where } X_i = \frac{x_i - x_i^l}{x_i^h - x_i^l}\ ,\ \text{Here } x_i = \Delta \propto_i$$

$$x_i^h = \Delta \propto_i^h = |19.68 - 10| + |10 - 9| + |12 - 9| = 13.68 \text{ for } [Ag - YSZ - CeO_2 - YBCO]$$

$$x_i^l = 3.2$$

The calculated values of U_i for different options and with Hastelloy as a substrate are given in Table 2. Similar values for different substrates (e.g. Hastelloy, nickel wire and silver wire) are given in Table 3.

Table 2
Multi-Attribute Analysis for Candidate Processes With Hastelloy as Substrate Based on Thermal Expansion Coefficient Mismatch

Options	*System*	$\Delta \propto_i x10^6 (K^{-1})$	U_i
E-Beam	HA/YSZ/YBCO*	3.2	1.00
SOL-GEL	HA/$LaAlO_3$/YBCO	3.2	1.00
MOCVD	HA/CeO_2/YSZ/YBCO	5.2	0.98
PLD	HA/YSZ/CeO_2/YBCO**	5.2	0.98
MOD	HA/$LaAlO_3$/YBCO	3.2	1.00
CVD	HA/$LaAlO_3$/YBCO	3.2	1.00
Aerosol/Spray Pyrolysis	HA/$LaAlO_3$/YBCO	3.2	1.00
Electrodeposition	HA/$LaAlO_3$/YBCO	3.2	1.00
Electro-phoresis	HA/$LaAlO_3$/YBCO	3.2	1.00

* Based on reference 21.

** Based on reference 12.

Table 3
Effect of Substrate Wire on $\Delta \propto_i$ and U_i

Options	***HA Wire***		***Ni Wire***		***Ag Wire***	
	$\Delta \propto_i x 10^6 (K^{-1})$	U_i	$\Delta \propto_i \times 10^6 (K^{-1})$	U_i	$\Delta \propto_i x 10^6 (K^{-1})$	U_i
E-Beam	3.2	1.00	5.3	0.98	11.68	0.59
SOL-GEL	3.2	1.00	5.3	0.98	11.68	0.59
MOCVD	5.2	0.98	7.3	0.92	13.68	0.00
PLD	5.2	0.98	7.3	0.92	13.68	0.00
MOD	3.2	1.00	5.3	0.98	11.68	0.59
CVD	3.2	1.00	5.3	0.98	11.68	0.59
Aerosol/Spray Pyrolysis	3.2	1.00	5.3	0.98	11.68	0.59
Electro-deposition	3.2	1.00	5.3	0.98	11.68	0.59
Electro-phoresis	3.2	1.00	5.3	0.98	11.68	0.59

4.1-2 Lattice Parameter Mismatch

In order to minimize the potential effects of dislocation and other defects brought about by the lattice dissimilarities between the substrate, buffer layer, and superconductor, the respective lattice constants should not vary by much. The multi-attribute merit/attribute for the lattice mismatch is calculated on the basis of the sum of the absolute of difference between the lattice constants of the individual layer. In doing so, the following approach was used to calculate the attribute/merit for the candidate options.

- DATA USED:

Substrates	***Lattice Parameter, L*** (Å)	***Reference No.***
Silver	a = 4.086	1
Ni	3.524	1
Hastelloy (C-276)	--	--
Buffer		
CeO_2	$\frac{a}{\sqrt{2}} = 3.826$	1
YSZ	$\frac{a}{\sqrt{2}} = 3.634$	1
$SrTiO_3$	a = 3.905	1
$LaAlO_3$	$\frac{a}{\sqrt{2}} = 3.793$	1
MgO	a = 4.21	1
Superconductor		
YBCO	a = 3.825	1

- Definitions of the Equations Used for Comparison:

$$x_i = |L_{Substrate} - L_{Buffer\ 2}| + |L_{Buffer\ 2} - L_{Buffer\ 1}| + |L_{Buffer\ 1} - L_{YBCO}| \ldots \text{for two Buffer Layers}$$

$$x_i = |L_{Substrate} - L_{Buffer\ 1}| + |L_{Buffer\ 1} - L_{YBCO}| \ldots \text{for one Buffer Layer}$$

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

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

$$x_i^l = |3.524 - 3.634| + |3.634 - 3.825| = 0.301 \ldots \text{for (Ni- YSZ- YBCO)}$$

$$x_i^h = |3.524 - 4.21| + |4.21 - 3.825| = 1.071 \ldots \text{for (Ni - MgO- YBCO)}$$

The calculated values of U_i for different options with nickel as a substrate are given in Table 4. Similar values for silver as a substrate are given and compared with the nickel values in Table 5.

TABLE 4
MULTI-ATTRIBUTE ANALYSIS FOR LATTICE PARAMETER "a"
WITH Ni SUBSTRATE

OPTIONS	*SYSTEM*	x_i	U_i
E-Beam	Ni/YSZ/YBCO	0.301	1.00
SOL-GEL	Ni/$LaAlO_3$/YBCO	0.301	1.00
MOCVD	Ni/CeO_2/YSZ/YBCO	0.685	0.87
PLD	Ni/YSZ/CeO_2/YBCO	0.303	1.00
MOD	Ni/$LaAlO_3$/YBCO	0.301	1.00
CVD	Ni/$LaAlO_3$/YBCO	0.301	1.00
Aerosol/Spray Pyrolysis	Ni/$LaAlO_3$/YBCO	0.301	1.00
Electrodeposition	Ni/$LaAlO_3$/YBCO	0.301	1.00
Electrophoresis	Ni/$LaAlO_3$/YBCO	0.301	1.00

Table 5
Effect of Substrate on x_i and U_i Based on
Lattice Parameter Mismatch

Options	***Ni Wire***		***Ag Wire***	
	x_i	U_i	x_i	U_i
E-Beam	0.301	1.00	0.643	0.90
SOL-GEL	0.301	1.00	0.325	1.00
MOCVD	0.685	0.87	0.643	0.90
PLD	0.303	1.00	0.645	0.89
MOD	0.301	1.00	0.325	1.00
CVD	0.301	1.00	0.325	1.00
Aerosol/Spray Pyrolysis	0.301	1.00	0.325	1.00
Electrodeposition	0.301	1.00	0.325	1.00
Electrophoresis	0.301	1.00	0.325	1.00

4.1-3 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}**** (mmHg)***
E-Beam	740	10^{-5}
SOL-GEL	800	760
MOCVD	600-850	1-10
PLD	900	0.2
MOD	25	760
CVD	750-900	20
Aerosol/Spray Pyrolysis	275-400	760
Electrodeposition	25	760
Electrophoresis	900	760

* From process flow sheets given in Figures 1-9 corresponding to the respective HTS coating operation.

- 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 $x_i = \left| T_i - T_{RT} \right|$

for Pressure Severity $y_i = \left| P_i - P_{atm} \right|$

where $T_{RT} = 25°C$ and $P_{atm} = 760$ mm Hg

$$X_i = \frac{x_i - x_i^l}{x_i^h - x_i^l} \text{ where } x_i^l = 0 \text{ and } x_i^h = 875\,^\circ\text{C}$$

$$Y_i = \frac{y_i - y_i^l}{y_i^h - y_i^l} \text{ where } y_i^l = 0 \text{ and } y_i^h = 760 \text{ mm Hg}$$

For Temperature Severity

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

For Pressure Severity

$$U_i^P = \sqrt{1 - Y_i^2}$$

For Overall Severity

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

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

The calculated values of the temperature severity, U_i^T and the pressure severity, P_i^T are given in Tables 6 and 7 respectively. The combined attribute/merit for the process severity calculated from these values U_i^T and U_i^P are given in Table 8 for the candidate options.

Table 6
Temperature Severity

Options	T_{op} *(°C)*	x_i	X_i	U_i^T
E-Beam	740	715.00	0.82	0.58
SOL-GEL	800	775.00	0.89	0.46
MOCVD	600	575.00	0.66	0.75
PLD	900	875.00	1.00	0.00
MOD	25	0.00	0.00	1.00
CVD	790	765.00	0.87	0.49
Aerosol/Spray Pyrolysis	275	250.00	0.29	0.96
Electrodeposition	25	0.00	0.00	1.00
Electrophoresis	900	875.00	1.00	0.00

Table 7
Pressure Severity

Options	P_{op} *(mm Hg)*	y_i	Y_i	U_i^P
E-Beam	0.00001	760.00	1.00	0.00
SOL-GEL	760	0.00	0.00	1.00
MOCVD	10	750.00	0.99	0.16
PLD	0.2	759.80	1.00	0.02
MOD	760	0.00	0.00	1.00
CVD	20	740.00	0.97	0.23
Aerosol/Spray Pyrolysis	760	0.00	0.00	1.00
Electrodeposition	760	0.00	0.00	1.00
Electrophoresis	760	0.00	0.00	1.00

Table 8
Combined Attribute/Merit Based on Process Severity for Candidate Options

Options	$U_i^T + U_i^P$	U_i
E-Beam	0.58	0.29
SOL-GEL	1.46	0.73
MOCVD	0.91	0.45
PLD	0.02	0.01
MOD	2.00	1.00
CVD	0.72	0.36
Aerosol/Spray Pyrolysis	1.96	0.98
Electrodeposition	2.00	1.00
Electrophoresis	1.00	0.50

4.1-4 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 organic 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 $YBa_2Cu_3O_7$ one would need 1 mole of Y-compound, 2 moles of Ba-compound, and 3 moles of Cu-compound.

- Regarding material utilization during coating application, all the vapor phase transport processes (e.g. MOCVD, PLD, E-Beam and CVD) were assumed to have a utilization efficiency of 15%. In other words, only 15% of the chemicals were utilized in coating the substrate/buffer composite and other 85% being lost to chamber walls or internals. 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 so on.

- 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 weight basis. All of them were then converted to a kilogram basis using the power factor method.

According to this method,

$$C = \propto (R)^{-\beta}$$

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

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

$\propto, \beta$ = Constants

Knowing the costs of a given chemical for two different shipment quantities, one can determine $\propto$ 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 9. Using these cost values and a utilization efficiency of 85% for the liquid/slurry phase transport system and 15% for the vapor phase transport system, the effective costs of producing YBCO coating were calculated. These costs are given in Table 10.

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:

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

$$x_i^l = \log\ (0.2) = -0.699, \text{ and}$$

$$x_i^h = \log\ (200) = 2.301$$

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

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

The resulting values of U_i for different options are given in Table 11.

TABLE 9
ESTIMATED COST OF PRODUCING YBCO FROM RESPECTIVE RAW MATERIALS FOR CANDIDATE OPTIONS

OPTION	*RAW MATERIAL INVOLVED*	*RAW MATERIAL PRICE $/gm*	*CALCULATED COST OF PRODUCING YBCO $/gm*
E-Beam	Y BaF_2 Cu	2.17 1.16 2.09	1.501
PLD and Electrophoresis	Y_2O_3 $BaCO_3$ CuO	3.65 1.28 0.24	2.083
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 $BaI_2 \cdot 2H_2O$ CuCl	2.13 5.50 2.11	8.61
Aerosol/Spray Pyrolysis and Electrodeposition	$Y(NO_3)_3$ $Ba(NO_3)_2$ $Cu(NO_3)_2 \cdot 6H_2O$	1.00 0.77 0.54	1.737
MOD	Y - acetate Ba - acetate Cu - acetate	1.08 2.30 3.39	4.976

TABLE 10
EFFECTIVE COST OF PRODUCING YBCO LAYER FOR CANDIDATE OPTIONS

OPTION	*ESTIMATED COST OF YBCO ($/gm)*	*MATERIAL UTILIZATION EFFICIENCY (%)*	*EFFECTIVE COST OF YBCO ($/gm)*
E-Beam	1.501	15	10.01
PLD	2.083	15	13.89
MOCVD	27.89	15	185.93
SOL-GEL	6.06	85	7.13
CVD	8.61	15	57.40
Aerosol/Spray Pyrolysis	1.737	85	2.04
MOD	4.976	85	5.85
Electrodeposition	1.737	85	2.04
Electrophoresis	2.083	85	2.45

TABLE 11
MULTI-ATTRIBUTE ANALYSIS FOR COST OF CHEMICALS AND MATERIAL UTILIZATION EFFICIENCY PARAMETERS

OPTION	*EFFECTIVE COST ($/gm)*	x_i	X_i	U_i
E-Beam	10.01	1.000	0.567	0.824
SOL-GEL	7.13	0.853	0.517	0.856
MOCVD	185.93	2.269	0.989	0.148
PLD	13.89	1.143	0.614	0.789
MOD	5.85	0.767	0.489	0.872
CVD	57.40	1.759	0.819	0.574
Aerosol/Spray Pyrolysis	2.04	0.310	0.336	0.942
Electrodeposition	2.04	0.310	0.336	0.942
Electrophoresis	2.45	0.389	0.363	0.932

4.1-5 Deposition Rate and Overall Thickness of Buffer Layer

The physical dimensions of the coating chamber used in applying the buffer layer(s) over the texturized metal substrate will be related to the deposition rate as well as the desired overall thickness.

These dimensions in general will be inversely proportional to the deposition rate and will be directly proportional to the thickness of the individual layer built in that chamber. As a result a combined parameter of “t/R” where t is thickness in Å and R is deposition rate in Å/sec was defined for multi-attribute analysis. The attribute/merit was calculated for such a parameter for the candidate options using the following approach:

- Data Used:

Options	$t_{buffer\ 1}$ (Å)	Ref. No.	$R_{buffer\ 1}$ (Å/s)	Ref. No.	$t_{buffer\ 2}$ (Å)	$R_{buffer\ 2}$ (Å/s)
E-Beam	100	21	2	21	--	--
SOL-GEL	4,000	4	30	4	--	--
MOCVD	100	22	0.667	22	1,400	1.167
PLD	1,000		0.06*		1,000	0.03*
MOD	4,000	**	30	**	--	--
CVD	4,000	**	30	**	--	--
Aerosol/Spray Pyrolysis	4,000	**	30	**	--	--
Electrodeposition	N/D	--	N/D	--	N/D	--
Electrophoresis	N/D	--	N/D	--	N/D	--

* Required data for PLD were estimated from the literature reported similar data for the E-Beam option using the following approach.
** Assumed for the $LaAlO_3$ layer based on reference 4.

It was assumed that

$$\left(\frac{R_{YSZ}}{R_{YBCO}}\right)_{E-Beam} = \frac{1.167\ \text{Å/s}}{100\ \text{Å/s}} = \left(\frac{R_{YSZ}}{R_{YBCO}}\right)_{PLD}$$

$$\therefore \left(\frac{R_{YSZ}}{R_{YBCO}}\right)_{PLD} = 0.01167$$

and for $R_{YBCO} = 5\ \text{Å/s}$

$$(R_{YSZ})_{PLD} = 0.06\ \text{Å/s}$$

Similarly, it was assumed that

$$\left(\frac{R_{CeO_2}}{R_{YBCO}}\right)_{E-Beam} = \frac{0.667\ \text{Å/s}}{100\ \text{Å/s}} = \left(\frac{R_{CeO_2}}{R_{YBCO}}\right)_{PLD}$$

$$\therefore \left(\frac{R_{CeO_2}}{R_{YBCO}}\right)_{PLD} = 0.00667$$

and for $R_{YBCO} = 5\ \text{Å/s}$

$$\left(R_{CeO_2}\right)_{PLD} = 0.03\,\text{Å/s}$$

For individual buffer layer, the thickness of1000 Å was used.

- Definition of the Equations Used for Comparison:

$$x_i = \log\left(\frac{t_{buffer\ 1}}{R_{bufer\ 1}} + \frac{t_{buffer\ 2}}{R_{buffer\ 2}}\right) \text{...for two buffer layers}$$

$$x_i = \log\left(\frac{t_{buffer\ 1}}{R_{buffer\ 1}}\right) \text{...for one buffer layer}$$

$$X_i = \frac{x_i - x_i^l}{x_i^h - x_i^l} \quad \text{where } x_i^l = \log\left(\frac{100}{30}\right) = 0.52$$

$$\text{and } x_i^h = \log(50,000) = 4.70$$

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

For the buffer layer thickness by the IBAD technique, Hammond(21) comments that 5000 Å has been required to get a high quality YBCO at Los Alamos National Laboratory. However, he thinks that 100 Å for buffer layer thickness may be sufficient; and therefore, for E-beam we have used a thickness of 100 Å. However, for the PLD option no such informatin is available; and therefore, we selected a value of 1000 Å which is in-between 100 Å and 5000 Å. The calculated values of the attribute/merit for each of the candidate options are given in Table 12.

Table 12
Multi-Attribute Analysis for Thickness and Deposition Rate of Buffer Layer(s)

Options	x_i	X_i	U_i
E-Beam	1.70	0.28	0.96
SOL-GEL	2.12	0.38	0.92
MOCVD	3.13	0.62	0.78
PLD	4.70	1.00	0.00
MOD	2.12	0.38	0.92
CVD	2.12	0.38	0.92
Aerosol/Spray Pyrolysis	2.12	0.38	0.92
Electrodeposition	N/D	N/D	N/D
Electrophoresis	N/D	N/D	N/D

(N/D = Not determined because of the literature reported inferior J_c values.)

4.1-6 Deposition Rate and Overall Thickness for YBCO

Using the same approach as used for the buffer layer deposition, the data for the YBCO were also analyzed. In this case no estimates were necessary to determine t and R values as available literature included the necessary values. The data used, equations defined for comparison and the resulting values of the attribute/merit are as follows:

- DATA USED:

OPTIONS	*THICKNESS OF SUPERCONDUCTOR COATING, t* (Å)	*Ref. No.*	*SUPERCONDUCTOR DEPOSITION RATE, R* $(\text{Å}/\text{s})$	*Ref. No.*
E-Beam	10,000	21	100	21
SOL-GEL	10,000	23	30	4
MOCVD	3,000	24	20	26
PLD	2,000	25	5	27
MOD	3,000	9	25	9
CVD	6,000	6	8.33	6
Aerosol/Spray Pyrolysis	10,000	8	1.389	8
Electrodeposition	N/D	--	N/D	--
Electrophoresis	N/D	--	N/D	--

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

- Definitions of the Equations Used for Comparison:

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

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

where $x_i^l = \log\left(\frac{2{,}000\,\text{Å}}{145\ \text{Å}/\text{s}}\right) = \log(13.79) = 1.14$ (based on Hammond' s paper, ref. 21)

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

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

The calculated values of the attribute/merit for each of the candidate option are given in Table 13.

TABLE 13
MULTI-ATTRIBUTE ANALYSIS FOR THICKNESS AND DEPOSITION RATE OF YBCO

Options	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 performance.)

4.1-7 Achieved Maximum Critical Current Density, J_c

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/cm^2 for the superconductor. 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 14. 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/cm^2 to $>10^6$ amp/cm^2 can be easily compared. The approach and the data used for the candidate options are as follows:

TABLE 14
LITERATURE REPORTED CRITICAL CURRENT DENSITY VALUES AS A FUNCTION OF DIFFERENT CONDUCTOR COATING TECHNIQUES

Conductor Coating Technique	Highest Jc Achieved (amp/cm2)*	Remarks	Reference No.
Sol-Gel	2.0×10^5	YBCO on YSZ with (100) Orientation	5
	1.9×10^4	Tl-1223 on Silver Foil	23
Metal Organic Chemical Vapor Deposition (MOCVD, CVD, PE-MOCVD, etc.)	5.0×10^6	YBCO on $LaAlO_3$ with (100) Orientation by PE-MOCVD	24
	2.3×10^6	YBCO on $LaAlO_3$ with (100) Orientation by MOCVD	28
	1.4×10^5	YBCO by LS-CVD on Platinum and Amorphous YSZ Prebuffer Layers (Deposited over Hastelloy C-276 Metal Substrate by Sputtering).	29
	6.3×10^6	YBCO on $SrTiO_3$ Single Crystal with (100) Orientation by TO-CVD	30
	2.0×10^4	YBCO on Polycrystalline Silver Foils by MOCVD	31
	2.5×10^5 (Unreproducible)	YBCO on Polycrystalline MgO Substrate by TC-CVD	32
Metal Organic Decomposition (MOD)	3.9×10^5	YBCO on $SrTiO_3$ with (100) Orientation by D-P Process	33
	1.0×10^3 (1.0×10^4 at 4K)	YBCO by Spin-Coating on Single Crystal of YSZ Using TFA Precursors	34
	- (5.0×10^5 at 4K)	YBCO by Spin-Coating on Single Crystal of $SrTiO_3$ with (100) and (110) Orientations Using TFA Precursors	34
	$>5.0 \times 10^6$	YBCO by Spin-Coating on Single Crystal of $LaAlO_3$ with (001) Orientation Using TFA Precursors	9
Electrodeposition	3.6×10^2 (4×10^3 at 4K)	YBCO on 9.5 mol % Y_2O_3 Stabilized Cubic Zirconia with (100) Orientation Using Nitrates	35
	- (3.96×10^3 at 4K)	YBCO on MgO Single Crystal with (100) Orientation Using Nitrates (under constant potential)	10
	- (5.1×10^3 at 4K)	Same as above except under Pulsed Potential	10
	- (5.0×10^2 at 4K)	YBCO on Nickel Strip/Wire and Silver Wire Using Nitrates	10
	2.0×10^4	TBCCO on Silver-Coated $SrTiO_3$ Single Crystal with (100) Orientation Using Nitrates (Under Constant Potential)	10
	5.6×10^4	Same as above except Under Pulsed Potential	10
Aerosol/ Spray Pyrolysis	3.0×10^4	YBCO on Polished MgO Substrate Using Aqueous Nitrates	8
Electrophoresis	$(1.0\text{-}2.0) \times 10^3$	Silver-Coated (Sheathed) YBCO on Nickel Alloy Wire	2

*J_c reported at 77K and under no field.

- DATA USED:

Options	***J_c Achieved x 10^{-6} (amp/cm^2)***
E-Beam	1-1.3
SOL-GEL	0.2
MOCVD	1-5
PLD	1-4
MOD	2-5
CVD	1-5
Aerosol/Spray Pyrolysis	0.03
Electrodeposition	0.02--0.056
Electrophoresis	0.001-0.002

- Assumption Made:

  The average value of J_c (of the range) is chosen for analysis.

- Definitions of the equations used for comparison:

$$x_i = \log_{10}\left(J_{c\,\text{avg}\,i}\right) \text{ where } J_{c\,\text{avg}} = \frac{J_{c\,\text{low}} + J_{c\,\text{high}}}{2}$$

$$X_i = \frac{x_i - x_i^l}{x_i^h - x_i^l} \text{ where } x_i^l = \log\left(3.6\times10^2\right) = 2.56 \ldots \text{Electrodeposition}$$

$$x_i^h = \log\left(6.3\times10^6\right) = 6.80 \ldots (\text{MOCVD})$$

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

The calculated values of the attribute/merit based on the achieved J_c values for candidate options are given in Table 15.

TABLE 15
MULTI-ATTRIBUTE ANALYSIS FOR LITERATURE REPORTED ACHIEVED J_C VALUES

Options	$J_{c\,avg} x10^{-6}$ (amp/cm^2)	**Log (J_C)**	X_i	U_i
E-Beam	1.15	6.06	0.83	0.44
SOL-GEL	0.2	5.30	0.65	0.24
MOCVD	3	6.48	0.92	0.62
PLD	2.5	6.40	0.91	0.58
MOD	3.5	6.56	0.94	0.66
CVD	3	6.48	0.92	0.62
Aerosol/Spray Pyrolysis	0.03	4.48	0.45	0.11
Electrodeposition	0.038	4.58	0.48	0.12
Electrophoresis	0.0015	3.18	0.15	0.01

4.1-8 Toxicity and Health Hazards

The health hazards related with the candidate manufacturing option depend on the toxicity of the raw materials used. The LD_{50} values of the chemicals associated with the respective process are used as 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, 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 is given as follows:

- Data Used:

Options	**Toxicity LD_{50} (mg/kg)**	**Toxic Compound Considered**
SOL-GEL	410	Lanthanum Nitrate Hexahydrate
MOD	11	Barium Acetate
CVD	265	CuCl
Aerosol/Spray Pyrolysis	8.5	Barium Nitrate
Electrophoresis	350	Y_2O_3

- Assumptions Made:

The most toxic substance from the several that are used in the given manufacturing 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:

$$\text{Highest toxicity} \equiv 0-50 \text{ mg/kg}$$
$$\text{Lowest toxicity} \equiv >5000 \text{ mg/kg}$$

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

$$X_i = \frac{x_i - x_i^l}{x_i^h - x_i^l} \qquad U_i = 1 - \sqrt{1 - X_i^2}$$

The calculated attributes/merits for the candidate options for which some data were available are given in Table 16.

TABLE 16
MULTI-ATTRIBUTE ANALYSIS FOR TOXICITY OF RAW MATERIALS/INTERMEDIATES USED IN HTSC MANUFACTURING OPTION

Options	X_i	U_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 said 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 represents the following characteristics:

1 - Highly favorable/acceptable all the times (very good).
2 - Favorable under certain circumstances (moderately good).
3 - Variable (good or bad).
4 - Unfavorable number of times (mostly bad).
5 - Highly unfavorable/unacceptable all the times (very bad).

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” in the field of HTS development. Similarly, related literature was also reviewed. Input on the subjective evaluation was received from the Oak Ridge National Laboratory (ORNL). This is shown in Table 17. The ORNL evaluation seems to emphasize more on the technical performance achieved rather than on the engineering and environmental criterions. An in-house prepared subjective evaluation at UTSI is shown in Table 18. 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.

Subsequently, a composite score was prepared for 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 19. 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 20.

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.

TABLE 17 (ORNL'S Evaluation)
Subjective Evaluation of Candidate Options for Manufacturing Long-Length HTS Wires/Tapes

Parameter	*Pulse Laser Deposition (PLD)*	*E-Beam*	*MOCVD*	*Solgel*	*CVD*	*Aerosol/Spray Pyrolysis*	*MOD*	*Electro-deposition*	*Electro-phoresis*
• 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 highly favorable/acceptable, very good, etc., at all the times.
2 - Means favorable under certain circumstances, moderately good, etc.
3 - Means variable (good or bad), cannot decide.
4 - Means unfavorable/unacceptable a number of times, mostly bad.
5 - Means highly unfavorable/unacceptable, very bad, etc., at all the times.

TABLE 18 (UTSI'S Evaluation)
Subjective Evaluation of Candidate Options for Manufacturing Long-Length HTS Wires/Tapes

Parameter	*Pulse Laser Deposition (PLD)*	*E-Beam*	*MOCVD*	*Solgel*	*CVD*	*Aerosol/Spray Pyrolysis*	*MOD*	*Electro-deposition*	*Electro-phoresis*
• 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 highly favorable/acceptable, very good, etc., at all the times.
2 - Means favorable under certain circumstances, moderately good, etc.
3 - Means variable (good or bad), cannot decide.
4 - Means unfavorable/unacceptable a number of times, mostly bad.
5 - Means highly unfavorable/unacceptable, very bad, etc., at all the times.

TABLE 19
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	53	61.0
Electrophoresis	70	48	59.0

TABLE 20
CALCULATED ATTRIBUTE/MERIT BASED ON COMPOSITE SCORE FROM SUBJECTIVE EVALUATION

Option	x_i = Score	$X_i = \frac{x_i - x_i^l}{x_i^h - x_i^l}$	$U_i = \sqrt{\left(1 - X_i^2\right)}$
PLD	56.0	0.487	0.874
E-Beam	54.5	0.467	0.884
MOCVD	67.0	0.632	0.775
SOL-GEL	64.5	0.599	0.801
CVD	70.0	0.671	0.741
Aerosol/Spray Pyrolysis	62.0	0.566	0.824
MOD	60.0	0.539	0.842
Electrodeposition	61.0	0.553	0.833
Electrophoresis	59.0	0.526	0.850

TABLE 21
PRELIMINARY RANKING OF THE CANDIDATE OPTIONS BASED ON OVERALL MERIT/UTILITY

OPTIONS	CALCULATED ATTRIBUTE/MERIT U_i										Calculated Overall Utility /Merit , U_o	Prelim. Rank
	Based on Thermal Expansion Coefficient Mismatch (a)	Based on Lattice Parameter Mismatch (a)	Based on Process-ing Temper-ature	Based on Process-ing Pressure	Based on Cost of Chemicals & Matl. Utilization Efficiency	Based on Coating Thickness & Deposit-ion Rate for Buffer	Based on Coating Thickness & Deposit-ion Rate for YBCO	Based on Achieved J_c Value	Based on Toxicity & Health Hazards	Based on Subjective Evaluation		
Assigned Weighting Factor, w_i	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	-0-	0.20		
E-Beam	0.98	1.00	0.58	0.0	0.82	0.96	0.95	0.44	N/D	0.88	0.749	4
SOL-GEL	0.98	1.00	0.46	1.00	0.86	0.92	0.86	0.24	0.30	0.80	0.792	2
MOCVD	0.92	0.87	0.75	0.05	0.15	0.78	0.93	0.62	N/D	0.77	0.661	6
PLD	0.92	1.00	0.0	0.02	0.79	0.0	0.85	0.58	N/D	0.87	0.590	7
MOD	0.98	1.00	1.00	1.00	0.87	0.92	0.94	0.66	0.04	0.84	0.905	1
CVD	0.98	1.00	0.49	0.23	0.57	0.92	0.78	0.62	0.25	0.74	0.707	5
Aerosol/ Spray Pyrolysis	0.98	1.00	0.96	1.00	0.94	0.92	0.13	0.11	0.03	0.82	0.768	3
Electro-deposition	0.98	1.00	1.00	1.00	0.94	N/D	N/D	0.12	N/D	0.83	N/D	--
Electro-phoresis	0.98	1.00	0.0	1.00	0.93	N/D	N/D	0.01	0.28	0.85	N/D	--

(a) Values taken for nickel wire.
N/D = Not Determined

PARAMETER	(w_i) ***Weighting Factor***
Processing Temperature	0.100
Processing Pressure	0.100
Thermal Expansion Coefficient Mismatch	0.100
Lattice Parameter Mismatch	0.100
Coating Thickness & Deposition Rate for Buffer	0.100
Coating Thickness & Deposition Rate for HTSC	0.100
Toxicity & Health Hazards(a)	--
Achievable Maximum J_c Value	0.100
Subjective Evaluation Score(b)	0.200
Cost of Chemicals/Material Utilization Efficiency	0.100
TOTAL	1.000

(a) Since toxicity and health hazards information are not available for the majority of the metal organics used, and since subjective evaluation included score for this, we have decided to exclude merit/utility for this particular parameter (at this time) until additional information becomes available.

(b) 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, preliminary ranking among the nine candidate options was developed. This rank as well as the respective option's overall utility/merit (U_o) are given in Table 21. As shown in Table 21, the top three candidate options from two different categories of applying buffer and HTSC materials include:

- From solution-growth techniques
    - Metal Organics Decomposition (MOD)
    - Sol-Gel
- From physical/vapor phase growth techniques
    - E-Beam

The corresponding highest J_c values reported for these three options from Table 14 are > 5.0×10^6 for MOD, 2.0×10^5 am/cm^2 for sol-gel and 1.3×10^6 amp/cm^2 for E-Beam. Thus, all these three options have demonstrated the potential of achieving acceptable high J_c values. 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 above preliminary ranking has 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 classified data were not available to us. Hence, it is possible that the ranking developed here may change in the future. The owners of such confidential data will at least have the knowledge of the methodology that was used here in developing this ranking. 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(21).

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 Å/sec)
A = Area of Deposition (usually in m^2)
t = Thickness of Deposit (usually in Å)
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 spliced into "m" equal splices 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:

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

and $$S_B = \frac{R_B\ L_B (N_P)_B}{(N_S)_B (t_s)_B}$$

and $$S_H = \frac{R_H \; L_H (N_P)_H}{(N_s)_H (t_s)_H}$$

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
$(t_S)_B$ = Thickness of deposit achieved per stage in buffer application section
R_B = Deposition rate for buffer layer

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 22 along with the similar values reported by Hammond(21). 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 top three candidates can be used in the future to determine the preliminary size and major specifications for the important components involved in the selected processes. However, until an additional experimental data base becomes available, such a preliminary estimation at present would be rather unreliable and of little use.

TABLE 22
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*
Buffer 1	MgO	$LaAlO_3$	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
Buffer 2	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			
Superconductor	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	0.833	1.389
L	3	1	0.9	0.4	3.6	2.16	2.16
Np	1	1	5	1	1	10	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 (A °/s)
L: Length (m)
Np: Number of Passes Per Stage
Ns: Number of Stages in Series
t:: Thickness of Coating (A °)

6.0 Economic Analysis

6.1 The purpose of this task is to perform cost analyses for promising manufacturing technologies for coated, high temperature superconductors. The objective is to perform life cycle cost analyses of the manufacturing facilities and establish the range of costs that may permit economic application of this technology. Of course, any commercial company contemplating producing this superconducting wire for eventual profit will conduct such analyses adapted to their particular company's circumstances and strategy. Nonetheless, this type of analysis will be useful in comparing the overall merits of different manufacturing processes and as a aid in evaluating the overall market competitiveness of the coated conductor versus powder-in-tube superconductors, low temperature superconductors or copper wire.

6.2 Methodology

The life cycle cost is the sum of capital charges, raw material costs and operating costs. This methodology follows the Electric Power Research Institute (EPRI) Technical Assessment Guide(36). Minor changes as are noted herein are required to apply this methodology to evaluate the potential investment in a manufacturing a plant rather than in a power plant, but they are conceptually the same. Capital costs are estimated for the land, buildings, and machinery necessary for the facility. This is the most difficult phase as it requires at least a conceptual design for the plant and equipment to be able to estimate costs. At the current status of technology for manufacturing coated conductors, there remains considerable uncertainty in the detailed processing equipment. Uncertainties can be treated by sensitivity analyses if desired. Once the total capital costs are determined, the annual charge is computed as a percentage of the total. This percentage factor is likely to be slightly different for each company, depending upon their individual circumstances, but several of the companies(37) in the HTS business indicated that a factor of about 22% is reasonable. This factor includes the charges shown in Table 23.

TABLE 23
COMPONENTS OF CAPITAL CHARGE RATE

Cost of Money (Interest)	9.9%
Federal Income Tax	4.0%
Depreciation (20 yr. S/L)	5.0%
Other Taxes	2.8%
Insurance	0.1%
Working Capital	0.2%
TOTAL	22.0%

A 20-year lifetime is assumed rather than the 30 years which would be more normal for a power plant. This is based on the presumption that coated conductor manufacturing is a new field and plant obselence is more likely than for a more mature technology.

Raw materials for the plant include the substrate, buffer layer(s), superconductor and final protective coating material. As noted in Section 3.0, these raw materials take many forms, depending on the application process under consideration.

Operating costs include labor and all its associated costs, utilities, sales expense, environmental expenses and other related costs.

6.3 Status of Cost Analyses

No complete cost analyses have been performed by UTSI to date. Believable cost estimates for production machinery have been difficult to obtain in part because most process work is proprietary. Dr. Robert Hammond has performed an analysis(38),(39) of an IBAD substrate with electron beam deposition of buffer layers and superconductor. His analysis provides estimated capital costs for this equipment and other valuable insights. As the work progresses on the nine (9) processes discussed earlier, cost estimates will be available to permit evaluation of respective production cost.

Some capital cost data that have been acquired indicate interesting trends. For example, cost quotes were obtained for two excimer lasers suitable for Pulse Laser Deposition (PLD) and two electron beam guns with accessories. These are listed in Table 24.

TABLE 24
COMPARISON OF LASER AND ELECTRON BEAM COSTS

SOURCE	*POWER ON TARGET (MAX.)*	*COST*	*COST/ WATT ON TARGET*
Lambda Physik Laser	50W	$140,000	$2,800/w
XMR, Inc. Laser	200W	$550,000	$2,750/w
K. J. Lesker Co. E-Beam	15Kw	$18,500	$1.23/w
Bakish, LTD E-Beam	100Kw	$350,000	$3.50/w

The difference in cost to vaporize the YBCO target between these two systems is noteworthy--almost 3 orders of magnitude higher for the pulsed excimer laser than for the electron beam. It has been pointed out by Hammond and others that use of higher power, continuous e-beams, even if physically deflected on the target, may not produce stoichiometric amounts of Y, Ba and Cu on the deposition surface. To solve this problem, he proposes to vaporize elemental Y, Ba, Cu targets while measuring the stoichiometry in the vicinity of the deposition site and controlling the deposition rate of each constituent individually. This requires some relatively complex instrumentation, but may be well worth the cost. Another question about high power electron beam vaporization for deposition is how fast the film can be deposited and still form the correct crystalline structure. Baring a major advance in modeling, the latter question will likely have to await experiments at high deposition rates.

Prices were requested from manufacturers of raw materials used in coated conductor manufacture. Some companies responded with estimates for prices in small (1kg) and large (1,000 kg) lots. Among the estimates received were those shown in Table 25.

TABLE 25
REPRESENTATIVE MATERIALS COST ESTIMATES

	1 Kg Lots	*1,000 Kg Lots*
YBCO	\$850/Kg	\$300/Kg
YBCO	\$595/Kg	\$195/Kg*
Y	\$978/Kg	\$345/Kg
Ba	\$354/Kg	\$125/Kg
Cu	\$116/Kg	\$41/Kg
Ce	\$1,116/Kg	\$394/Kg
CeO_2	\$346/Kg	\$122/Kg

* In 2,000 Kg Lots

The draft *Development Plan for Coated Conductor Commercialization* under consideration has the following goals (among others):

Current Density, J_c, with 5T Field	1×10^6 amps/cm^2
Engineering Current Density, J_e	1×10^5 amps/cm^2
Current Carrying Capacity	200 amps
Cost	≤ \$10/K amp meter

For a conductor that meets the above goals and is 1 cm wide and 2 microns thick, assuming a 14% material application efficiency, the YBCO cost is \$0.92-\$1.40/KAM, depending on which price is used. Using similar assumptions, a 200Å CeO_2 buffer layer material cost would be \$.003/KAM. These materials costs plus the cost of the textured substrate and the protective coating are not prohibitive to meeting the cost goals, but are significant enough for close consideration of materials utilization.

7.0 Development of Real Time Process Control Using *In-Situ* Diagnostics

The various HTSC coated conductor manufacturing processes will each require specialized process control measurements. Potential technologies capable of making the needed measurements need to be identified and investigated. To understand process control needs, analyses of each of the different manufacture processes are being carried out to determine the types, ranges, accuracies, etc. of required process control measurements. A search for methods useful for characterizing the quality of the various layers of coated conductors is also being undertaken.

7.1 Process Control Tables

The measurements needed in each process were determined from the process flow schemes given earlier and from literature surveys(20,40-42), which were undertaken to develop a thorough understanding of each process and a comprehensive tabulation of the control parameters. After the process review, a preliminary worksheet for each process was created to provide a general description of the kinds of measurements needed as well as noting the parameter ranges when available from the literature. After a satisfactory worksheet for each process was completed the information was placed in the form of a table. The resulting partially completed tables follow. The table for each process has six columns denoted “item”, “measurement”, “range”, “accuracy”, “technology”, and “comments”. The “item” column identifies the components or sub-processes, such as dissolver or e-beam based YSZ application (see MOCVD Method table). The “measurement” column describes what specific measurements will be needed for that item, such as temperature or pressure. The “range” and “accuracy” columns give specifications for the measurement. The information in the “measurement”, “range”, and “accuracy” columns suggests a measurement technique which is presented in the “technology” column. The “comments” column provides questions or comments pertinent to that item. Eventually, costs for the measurements will be included in a new “cost” column.

At the current time these tables provide only some of the necessary information due to the ongoing development of the manufacturing processes and the lack of process details in the open literature. Once completed, these tables will provide valuable information in the further development of the methods by describing processing parameters that must be considered and controlled for the various manufacturing methods.

The MOCVD Method is discussed as an example of the process tables. The first item identified in the table is the substrate. Since a high quality superconductor requires a high quality substrate, it is expected that the substrate quality will require monitoring. The measurements prescribed, such as crystal orientation and morphology, would be needed to properly characterize the substrate quality. Another item listed in the MOCVD Table is the heated piping containing the organic precursor solutions of yttrium, barium, and copper, which must be heated to appropriate temperatures to ensure evaporation and prevent condensation. The different layer applications, such as the e-beam based YSZ and CeO_2 applications and the MOCVD-based HTSC application, also appear in the items column. Pressure, temperature, and deposition rates are some measurements that must be monitored during these applications. The table also identifies process points where measurements such as layer thickness, crystal orientation, and composition of new film layers are required to control layer deposition and ensure quality. The final oxidation/annealing and cooling steps are shown in the table as subprocesses requiring monitoring and control of temperature, time, and oxygen pressure.

At the end of the MOCVD Method table, two items are included which are not part of the process designs at present. These items are post manufacture testing and a wire marking system. The post manufacture testing would provide quality control via a thermal quench of the product and measurement of electrical characteristics. The wire marking system is included to mark any defect locations detected during manufacture for the purpose of post manufacture processing to remove defective regions. Post manufacture testing and the wire marking system have been included in all of the process control tables.

TABLE 26
MOCVD METHOD PROCESS CONTROL

Item	Measurement	Range	Accuracy	Technology	Comments
Substrate	crystal orientation				
	morphology				
	geometry				
	grain size				
Annealing Furnace	temperature	900 °C			
Precursor ovens for Y, Ba, Cu - TMHD	temperature	Y-130-160 °C Cu-130-160°C Ba-260°C (43,45)			The pipes containing the Y, Ba, Cu-TMHD must be temperature controlled with heat pipes to temperature at least equal to highest evaporation temperature so the chemicals don't condense back. (43)
Pipes inside the gas handling system	temperature	300 °C (45)		heating tapes	To avoid premature condensation of the precursors.
Dissolver	flow rate of nitrogen	150 cm^3/min (44)		mass flow controller	Is this a batch or continuous process?
	flow rate of Y(TMHD)$_3$	75 cm^3/min (45)		mass flow controller	
	flow rate of Ba(TMHD)$_2$	600 cm^3/min (45)		mass flow controller	
	flow rate of Cu(TMHD)$_2$	80 cm^3/min (45)		mass flow controller	
	chemical flow rates				
	level				
	temperature	300° C (45)			
Vaporizer	temperature	230 °C			
	flow rates of chemicals				
E-Beam Based CeO_2 Application	tape temperature				What are the off-gasses?
	flow rate of off-gasses				
	flow rate of H_2/N_2 mix				
	pressure				
	deposition rate	0.0667 nm/s			
CeO_2 Block	thickness				When does the block need to be replaced?
	quality				Is the block assumed to be purchased?
Film - after CeO_2 application	layer thickness	10 nm			
	crystal orientation				
	composition				
	morphology				
	geometry				
	grain size				
Electron Gun	power				
	location on target				
E-Beam Based YSZ Application	tape temperature				
	pressure				
	deposition rate	0.1167 nm/s			
YSZ Block	thickness				When does the block need to be replaced?
	quality				Is the block assumed to be purchased?
Film - after YSZ application	layer thickness	140 nm			
	crystal orientation				
	composition				
	morphology				
	geometry				
	grain size				
MOCVD - Based HTSC Application	temperature	600-850 °C			What are the vapors?
	pressure	1-10mm Hg			
	deposition rate	2 nm/s			
	film temperature	780 °C (45)			
	transport line temperature				
	flow rate of vapors				
Plasma Tube	flow rate of chemicals				
Film - after HTSC application	layer thickness	300 nm			
	crystal orientation				
	composition				
	morphology				
	geometry				
	grain size				
Oxidation/Annealing	temperature	400-680 °C		temperature controller	What are the off-gasses?
	time			temperature controller	
	pressure of O_2	100 mm Hg			
	flow rate of off-gasses				
Cooling	temperature	680-25 °C		temperature controller	What are the off-gasses?
	time	13 hours (44)		temperature controller	
	pressure of O_2	100 mm Hg			
	flow rate of off-gasses				
Post Manufacturing Test	quenching and I/V characteristics				
Wire Marking System	wire defects				
Global Measurements	speed of ribbon				The speed of the ribbon should control the processing time.
	tension				
	length of ribbon onto spool				
	CEM (cont. emissions monitoring)				

TABLE 27
Aerosol/Spray Pyrolysis Method

Item	Measurement	Range	Accuracy	Technology	Comments
Substrate	crystal orientation				
	composition				
	morphology				
	geometry				
	grain size				
Dissolver	flow rates of chemicals				Nitrates should have 2% concentration (8)
Sprayers	temperature	275 - 400 °C	1% (8)		There are no furnace gradients.
	flow rate of O_2 and N_2	4 l/min (8)			
	deposition rate	138.9 µm/s			
	aqueous nitrates solution delivery rate	1-2 ml/min (8)			O_2/N_2 are in a combined flow.
	drain/excess spray control monitor				
Film - after each sprayer	layer thickness				Final layer thickness of 1000 nm.
	layer quality				
Preheater	temperature	600 - 800 °C			What are the off-gasses?
	flow rate of off-gasses				
	flow rate of air				There are no furnace gradients.
Film - after each preheater	crystal orientation				
	composition				
	morphology				
	geometry				
	grain size				
Heater	temperature	850 - 900 °C		temperature controller	What are the off-gasses?
	flow rate of oxygen and nitrogen	4 l/min (8)			
	flow rate of off-gasses				
	time	2 hours (8)		temperature controller	
Oxidizer/Cooler	temperature	500 - 25 °C		temperature controller	What are the off-gasses?
	time			temperature controller	Cooling rate of 40 C/min. (8)
	flow rate of oxygen	4 l/min (8)			
	flow rate of off-gasses				
Post Manufacturing Test	quenching & I/V characteristics				
Wire Marking System	wire defects				
Global Measurements	speed of ribbon				The speed of the ribbon should control the processing time.
	tension				
	length of ribbon onto spool				
	CEM (continuous emissions monitoring)				

TABLE 28
CVD Method

Item	Measurement	Range	Accuracy	Technology	Comments
Substrate	crystal orientation				
	composition				
	morphology				
	geometry				
	grain size				
Vaporizer #1	temperature of YCl				What states are the chemicals in? Are any of the chemicals corrosive?
	temperature	820 °C			
	flow rates of chemicals				
	pressure				
Vaporizer #2	temperature of BaI	150 °C (6)			What states are the chemicals in? Are any of the chemicals corrosive?
	temperature	950 °C			
	flow rates of chemicals				
	pressure				
Vaporizer #3	temperature of CuCl				What states are the chemicals in? Are any of the chemicals corrosive?
	temperature	340 °C			
	flow rates of chemicals				
	pressure				
Chambers	temperature of pipes to chamber	250 °C (41)			
	deposition rate	83.3 µm/s			
	temperature	750 - 900 °C			
	pressure	20 mm Hg			
	flow rate of oxygen	200 sccm (6)			
	flow rate of precursor				
Film - after each chamber	layer thickness				Final layer thickness is 600 nm.
	crystal orientation				
	composition				
	morphology				
	geometry				
	grain size				
Bubbler	temperature	20 °C			Probably will not need to know the flow rate of the water. Oxygen/water ratio of 1/7. (6)
	flow rates of chemicals				
	level control of water				
Oxidizer/Cooler	temperature	500 - 25 °C		temperature controller	What are the off-gasses? Are the off-gasses corrosive?
	time	48 hours (6)		temperature controller	
	flow rate of oxygen				
	flow rate of off-gasses				
Post Manufacturing Test	quenching & I/V characteristics				
Wire Marking System	wire defects				
Global Measurements	speed of ribbon				The speed of the ribbon should control the processing time.
	tension				
	length of ribbon onto spool				
	CEM (continuous emissions monitoring)				

TABLE 29
Electrodeposition Method

Item	Measurement	Range	Accuracy	Technology	Comments
Substrate	crystal orientation				
	composition				
	morphology				
	geometry				
	grain size				
Dissolver	flow rate of chemicals				Ba, Cu, Y-nitrates are powders. $AgNO_3$ and HNO_3 are liquids.
	time				
	temperature				
Mixer	flow rates				
	level				
	time				
	quality				
Electrolytic Cell	current density	12 mA/cm^2 (11)			
	voltage	-300 to -500 V (11)			
	composition of electrolyte				
Film - after cell	layer thickness				
	layer quality				
Dryer	temperature	150 °C			What are the off-gasses?
	time				
	flow rate of off-gasses				
Film - after Dryer	crystal orientation				
	composition				
	morphology				
	geometry				
	grain size				
Thermal Treatment	temperature	900-500 °C		temp. controller	What are the off-gasses? O_2 and N_2 are in a combined flow.
	time			temp. controller	
	flow rate of oxygen and nitrogen				
	flow rate of off-gasses				
Oxidizer/Cooler	temperature	500-25 °C		temp. controller	What are the off-gasses?
	time			temp. controller	
	flow rate of cold oxygen				
	flow rate of off-gasses				
Post Manufacturing Test	Quenching & I/V characteristics				
Wire Marking System	wire defects				
Global Measurements	speed of ribbon				The speed of the ribbon should control the processing time.
	tension				
	length of ribbon onto spool				
	CEM (cont. emissions monitoring)				

TABLE 30
Electrophoresis Method

Item	Measurement	Range	Accuracy	Technology	Comments
Substrate	crystal orientation				
	morphology				
	geometry				
	grain size				
Mixer	flow rates				
	time				
Calciner	temperature	800 - 860 °C (46)		temperature controller	Are there off-gasses?
	time	24 hours (46)		temperature controller	
Pulverizer	flow rate				
	temperature	100 °C			
	particle size				
Slurry Mixers	flow rates				
	levels				
Electrophoresis Chambers	temperature	20 °C (46)	± 4 °C (46)		Are any of the chemicals corrosive?
	current density	5-50 µA/cm^2 (46)			
	voltage	150 V (46)			
	magnetic field	8 T (46)			
	deposition rate	1 - 5 µm/min (46)			
Film (after each chamber)	layer thickness				
	layer quality				
Sintering Furnaces	temperature	900 °C	± 4 °C (46)		What are the off-gasses? Are O_2 and N_2 in individual flows or a combined flow? Are the off-gasses corrosive?
	flow rates of O_2 and N_2				
	oxygen/nitrogen ratio				
	flow rate of off-gasses				
Film - after each furnace	crystal orientation				
	composition				
	morphology				
	geometry				
	grain size				
Oxidizer/Cooler	temperature	500°C cooled to 25 °C	± 4 °C (46)	temperature controller	What are the off-gasses? Are the off-gasses corrosive?
	time	8 hours (46)		temperature controller	
	flow rate of oxygen				
	flow rate of off-gasses				
Post Manufacturing Test	Quenching & I/V characteristics				
Wire Marking System	wire defects				
Global Measurements	speed of ribbon				The speed of the ribbon should control the processing time.
	tension				
	length of ribbon onto spool				
	CEM (continuous emissions monitoring)				

TABLE 31
E-Beam Based Conductor Coating Method Utilizing IBAD Technique for Buffer Application

Item	Measurement	Range	Accuracy	Technology	Comments
Hastelloy Tape	morphology				
	geometry				
Ion Gun	power				
	energy	300 eV (47)			
	current density	200 μA/cm^2 (47)			
	flow rate of argon gas				
E-Beam Based YSZ IBAD Deposition	pressure	4x10^{-4} mm Hg			What are the off-gasses? Deposition carried out at room temp. but the substrate temp. rises. (48) Ion beam must be at 53° angle to the tape. (49)
	flow rate of off-gasses				
	flow rate of O$_2$				
	deposition rate	.2 nm/s (49)	1% (50)	atomic absorption monitor (50)	
	substrate temperature	60-100°C (47,48)			
YSZ Block	thickness				When does this block need to be replaced?
	quality				
Electron Gun	power				
	location on target				
Film - after YSZ deposition	layer thickness	10 nm (49)			
	crystal orientation				
	composition				
	morphology				
	geometry				
	grain size				
E-Beam Based YBCO Deposition	pressure	10^{-5} mm Hg			What are the off-gasses?
	flow rate of off-gasses				
	flow rate of oxygen	2220 sccm (49)	1%	mass flow controller	
	deposition rate	10 nm/s	1% (50)	atomic absorption monitor (50)	
	substrate temperature				
	atomic absorption rate of Y, Ba, Cu		1% (50)	atomic absorption monitor (50)	
Film - during YBCO deposition	layer thickness	1 μm			
	crystal orientation				
	composition				
	morphology				
	geometry				
	grain size				
YBCO Sources	thickness				When does this block need to be replaced?
	quality				
Atomic Oxygen Generator	power				
	flow rate of oxygen				
Post Manufacturing Test	quenching & I/V characteristics				
Wire Marking System	wire defects				
Global Measurements	speed of ribbon	3-25 cm/sec (49)			The ribbon speed should control processing time.
	tension				
	length of ribbon onto spool				
	CEM (cont. emissions monitoring)				

TABLE 32
MOD (Metalorganic Deposition)

Item	Measurement	Range	Accuracy	Technology	Comments
Substrate	crystal orientation				
	composition				
	morphology				
	geometry				
	grain size				
Dissolver	flow rates of chemicals				Acetates are solid, acid is liquid. The chemicals are corrosive.
	levels				
	temperature				
Dryer	time				This is a continuous process. What is the state of the output chemicals? Is time sufficient to control quality or is a closed loop required? The chemicals are corrosive.
	temperature	80 °C			
Dip coaters	levels				The chemicals are corrosive.
	flow rate of precursor solution				
	deposition rate	2.5 nm/s			
	temperature				
	composition of material in tank for quality				
Film - after each dip coater	layer thickness				Final thickness of 300 nm.
	layer quality				
Ovens	temperature	200-400°C			What are the off-gasses? The off-gasses are corrosive.
	flow rate of oxygen				
	pressure of off-gasses				
Film - after each oven	crystal orientation				
	composition				
	morphology				
	geometry				
	grain size				
Decomposer	temperature	850 °C			Gasses are in a combined flow. The off-gasses are corrosive. What is the composition of the off-gasses?
	flow rates of chemicals				
	time				
Oxidizer/Cooler	temperature	25 °C from 500 °C		temperature controller	The off-gasses are corrosive. What is the composition of the off-gasses?
	flow rate of oxygen				
	time			temperature controller	
Post Manufacturing Test	Quenching and I/V characteristics				
Wire Marking System	wire defects				
Global Measurements	speed of ribbon				The speed of the ribbon should control the processing time.
	tension				
	length of ribbon onto spool				
	CEM (Continuous Emissions Monitoring)				

TABLE 33
PLD Method

Item	Measurement	Range	Accuracy	Technology	Comments
Substrate	crystal orientation				
	morphology				
	geometry				
	grain size				
Mixer	flow of incoming powders				Is this a batch process?
	time				
Calciner	temperature	930 °C			Is this a batch process? Are there any off'-gasses, perhaps CO$_2$?
	time	24 hours			Should there be a flow of oxygen?
Pulverizer	temperature				What type of pulverizer is this?
	time				Is this a batch process?
	flow rate of air				
	particle size				
Annealing Furnace	temperature	900 °C			
Pulsed-Laser Based YSZ Application	pressure	.2 mm Hg			What are the off-gasses?
	flow rate of gas mixture				
	deposition rate	.169 nm/s	1% (50)	atomic absorption monitor (50)	
	tape temperature				
YSZ Block	thickness				When does the block need to be replaced?
	quality				
Laser Beam Generator	power				
	rep rate	100 Hz			
	location on target				
Substrate - after YSZ application	layer thickness	100 nm			
	crystal orientation				
	composition				
	morphology				
	geometry				
	grain size				
Pulsed-Laser Based CeO$_2$ Application	pressure	.2 mm Hg			What are the off-gasses?
	flow rate of gas mixture				
	tape temperature	900 C			
	deposition rate	96.7 µm/s	1% (50)	atomic absorption monitor (50)	
CeO$_2$ Block	thickness				When does the block need to be replaced?
	quality				
Substrate - after CeO$_2$ application	layer thickness	100 nm			
	crystal orientation				
	composition				
	morphology				
	geometry				
	grain size				
Pulsed-Laser Based YBCO Application	pressure	.2 mm Hg			What are the off-gasses?
	flow rate of gas mixture				
	tape temperature	800 °C			
	deposition rate	3 nm/s (49)	1% (50)	atomic absorption monitor (50)	
YBCO Block	thickness				Does the YBCO block need to be sintered and annealed?
	quality				When does the block need to be replaced?
Post Manufacturing Test	quenching & I/V characteristics				
Wire Marking System	wire defects				
Global Measurements	speed of ribbon				The speed of the ribbon should control the processing time.
	tension				
	length of ribbon onto spool				
	CEM (continuous emissions monitoring)				

TABLE 34
Sol-Gel Method

Item	Measurement	Range	Accuracy	Technology	Comments
Substrate - RABIT Ni-rich tape before first buffer dip coater	crystal orientation				
	morphology				
	geometry				
	grain size				
Dissolvers	flow rates of chemicals				What state are the chemicals in? Are any of the chemicals corrosive?
	time				
	level				
	pressure				
Reflux Distillation #1	flow rates of chemicals				What is the composition of the alcohol mixture going to recovery?
	temperature	124 °C			
	time				
	level				
	pressure				
Reflux Distillation #2	flow rates of chemicals				What is the composition of the alcohol mixture going to recovery?
	temperature				
	time				
	level				
	pressure				
Dilution	flow rates of chemicals				
	level				
	temperature				
	pressure				
Partial Hydrolizer	flow rates of chemicals				Are water and alcohol in individual flows or a combined flow?
	level				
	temperature				
	pressure				
Buffer Dip Coaters	level of precursor gel				
	deposition rate	3 nm/s			
	temperature				
Substrate - after each buffer dip coater	layer thickness				Final thickness of 400 nm.
	layer quality				
Pyrolizers	temperature	800 °C			What are the off-gasses? Are the off-gasses corrosive?
	flow rate of oxygen				
	flow rate of off-gasses				
Substrate - after each pyrolizer	crystal orientation				
	composition				
	morphology				
	geometry				
	grain size				
Dissolvers	flow rates of chemicals				What state are the chemicals in? Are any of the chemicals corrosive?
	time				
	level				
	pressure				
Mixer	flow rates of chemicals				
	level				
	time				
	pressure				
	temperature				
Vaccuum Distillation	flow rates of chemicals				Are any of the chemicals corrosive?
	pressure				
	time				
	level				
	temperature				
Organic Solution of Precursor	flow rates of chemicals				Are any of the chemicals corrosive?
	level				
	time				
	temperature				
Precursor Dip Coaters	levels of YBCO precursor solution				May not be necessary to monitor temperature.
	deposition rate	3 nm/s			
	temperature				
Film - - after each dip coater	layer thickness				Final thickness of 1000 nm.
	layer quality				
Pyrolyzers	temperature	400 °C			What are the off-gasses?
	flow rate of oxygen				
	flow rate of off-gasses				
Film - - after each pyrolyzer	crystal orientation				
	composition				
	morphology				
	geometry				
	grain size				
Thermolyzer	temperature	700 - 850 °C		temperature controller	Oxygen and nitrogen are in a combined flow. What are the off-gasses?
	flow rates of oxygen and nitrogen				
	flow rate of off-gasses				
	time			temperature controller	
Oxidizer/Cooler	temperature	500 - 25 °C		temperature controller	What are the off-gasses?
	flow rate of oxygen				
	flow rate of off-gasses				
	time			temperture controller	
Post Manufacturing Test	quenching & I/V characteristics				
Wire Marking System	wire defects				
Global Measurements	speed of ribbon				The speed of the ribbon should control the processing time.
	tension				
	length of ribbon onto spool				
	CEM (cont. emissions monitoring)				

7.2 Layer Quality Assessment

A second task in development of process control is characterization and quality assessments of the substrate and conductor layers. Two technologies are actively being investigated for this purpose: scatterometry and Raman spectroscopy. Study of scatterometry was undertaken due to its potential for surface roughness measurement while Raman spectroscopy is being studied as a means of measuring crystal composition and orientation.

Surface Roughness

High quality epitaxial growth of superconducting layers on subtrates prepared by processes such as RABiTS require smooth substrates suggesting need for quantifying surface roughness. Atomic force microscopy measurements of RABiTS substrates(42) have shown rms surface roughnesses of 50 nm approaching the smoothness of optical quality surfaces (normally less than 10 nm). While such a surface would be considered a good reflector exhibiting primarily specular reflection, it would also show significant diffuse scatter. During the last quarter, research was conducted to assess the potential of determining surface roughness using scatterometers. Scatterometers are composed of illumination sources (frequently lasers), sample holders, gonimeters, and detector electronics.

Measurement of the radiation scattered from a surface can be used to determine many surface roughness parameters such as arithmetic average roughness (s_a), rms roughness (s), average and rms slope parameters (m_a and m), and surface wavelength ($l = 2ps/m$). These parameters can be obtained from the surface power spectral density (PSD) which describes the surface height variations in terms of surface spatial frequencies. The measurable bidirectional scatter distribution function (BSDF), or specifically for a reflective surface the bidirectional reflection distribution function (BRDF), is related to the surface PSD. Thus measurement of the BSDF allow calculation of surface roughness statistics. The BSDF is the ratio of scattered power (specifically radiance) to illuminating power (or irradiance). It is bidirectional since both the incident and scatter direction are pertinent. The BRDF is also generally two dimensional (i.e. light is scattered into all directions of the hemisphere above the reflecting surface) since the surface itself is two dimensional though the BRDF for an isotropic surface will not depend on the azimuthal angle.

Raman Spectroscopy

Raman spectroscopy can give information directly and accurately by measuring vibrational modes in the crystal.(51-56) A Raman spectroscopy experimental setup is given in Figure10.

In studying the composition of the HTSC, oxygen content must be determined. The critical temperature of $YBa_2Cu_3O_{7-x}$ films is dependent upon the oxygen content, which can be monitored with Raman spectroscopy. By observing the 500 cm^{-1} in the proper polarization the oxygen content can be found.(53, 55-58)

Crystal orientation can also be obtained by observing several Raman spectra of the HTSC film. By applying different polarizations to the laser, using different orientations of the crystal axes and studying different places on the film an accurate measurement can be made of the crystal orientation.(58-61) For example, by comparing the relative intensities of the 500cm^{-1} line and the 335 cm^{-1} line in the proper Raman mode the degree of c-axis tilting away from the normal can be determined.(60)

The main difficulty with Raman spectroscopy is the data acquisition speed. Raman spectroscopy must provide real time measurements to be used in a processing environment. With some technique development, real time measurements should be possible under the appropriate conditions.(52, 58)

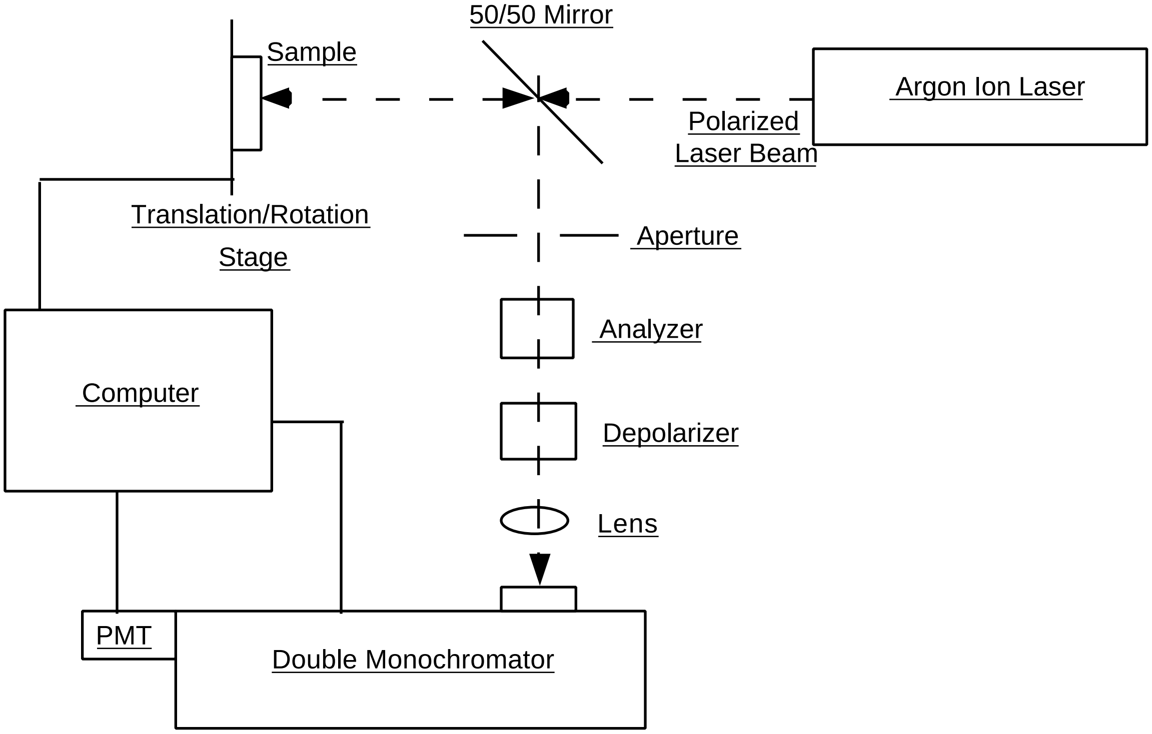


Figure10. Raman Spectroscopy Setup

8.0 Major Concerns/Issues and Datagap for the Selected Three Candidates

In order to scale-up the current know-how on the selected three candidates to commercially viable processes to manufacture long-lengths of coated conductor wires/tapes, a significant amount of development work is needed. Areas of major technical concerns/issues and significant gaps in the useful data for each of these candidate options are as follows.

8.1 E-Beam

Robert Hammond and his co-workers at the Stanford University(21) have provided a very useful and critical review of the concerns and issues related to this option. Following list includes some additional concerns.

8.1-1 IBAD Related Technical Issues

Some of the most important technical issues related to the IBAD process include:

- 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, and
- Possible requirement for a buffer layer between the IBAD layer and the YBCO layer to improve lattice matching.
- 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^+ ions 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 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.

8.1-2 YBCO Deposition Related Technical Issues

Some of the technical issues related to YBCO deposition using E-beam include:

- YBCO composition related --

  YBCO is a line compound--it is superconducting only with the 1-2-3 stoichiometry. Nevertheless according to Hammond(21), the material can be several percent rich in Y or Cu without showing any degradation in T_c or perhaps even in J_c. Excess barium content degrades the superconducting properties. It will be 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.

- Oxygen requirement related--

  According to Hammond's estimate(21), to grow YBCO in-situ at the rate of 100 A°/sec, one would require 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 4×20^{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. Also, Hammond claims that Y and Ba deposited on the walls of the chamber will react with a significant amount of oxygen atoms, and therefore, a pumping requirement to maintain the low pressure(of the order of10^{-5}mm Hg) in the chamber may be feasible. However, this also needs to be demonstrated.

- High-Rate, Large-Area Deposition related--

  The YBCO deposition process must be able to operate at rates approaching ~100 A°/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. Similarly, whether YBCO should be produced in-situ from Y-, Ba- and Cu- sources inside the chamber, or should be produced outside and then brought in, needs to be ascertained. On-line diagnostic and control systems for such a deposition chamber need to be developed and tested.

Another important concern is identifying the suitable recovery/treatment/disposal system(s) for the off-gases and for the wall/internal deposits. Using BaF_2 as a source for Barium will release fluorine-containing species in the off-gases. Whether corrosion-resistant material will be needed for the chamber as well as other accessories etc. has to be determined.

8.2 Sol-Gel

In the scheme developed by us and presented earlier, it is shown that the texturized substrate would be obtained from a RABiTS technique applied to an Ni-rich alloy tape. Such a texturized substrate would be then used to apply a coating of suitable buffer layer (e.g. $LaAlO_3$) by the sol-gel method. The resulting composite would then be used to apply the coating of YBCO precursors by the sol-gel method also. The coated tape is then wound on a spool and goes through the thermal treatment in a batch or semi-batch mode. Thus, the major steps involve, preparation of texturized substrate by the RABiTS method, and coating of the buffer and YBCO precursors by the sol-gel method. Most of the technical information on the RABiTS technology is proprietary and therefore, not available in the open literature. However, the following concerns are believed to need appropriate attention.

8.2-1 RABiTS Related Technical Issues

- Acceptable Quality of Texturized 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. In general, texturized 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. texturized) 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 treatment may not be possible, and therefore, an alternative scheme for rolling and annealing may be needed.

8.2-2 Sol-Gel Related Technical Issues

- 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(63) 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 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, a batch or semi-bath 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 details to address such needs.

- Other simplifying or cost-savings measures that need to be evaluated include:

  - Using N_2 as an inert gas instead of Ar.
  - Using simple and cheaper chemicals to prepare precursors gel/solution.

8.3 MOD

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 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 organic 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 simpler than the one used for the sol-gel scheme and still needs to be evaluated for possible simplification using common reagents. It is possible that if organometallic salts are used as carboxylates (e.g. acetates) that some unwanted carbonate such as $BaCO_3$ 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, 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.

9.0 Conclusions and Recommendations

As a result of our evaluation of the candidate options, we have reached more or less the similar conclusions that the others in the field have reached. 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 and E-Beam based options as three 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 ranking developed at present may change.

For the selected three candidates, various technical issues are discussed earlier, however, categorically they 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.) rate 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, 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 protection layer--

  No work has been reported that deals with the outside protective/insulating 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 will be of unacceptable quality. As a result, need will 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 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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