DOE/PC95231-31

FINAL TECHNICAL REPORT
FOR
UTSI/CFFF MHD PROGRAM COMPLETION AND RELATED ACTIVITY

Report Period Start Date:	**September 15, 1995**
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DISCLAIMER

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EXECUTIVE SUMMARY

In this final technical report, UTSI summarizes work completed under DOE Contract No. DE-AC22-95PC95231. This work began on the contract effective date, September 15, 1995 and is continuing on a very small basis to complete the groundwater remediation as of this date.

The work scope required UTSI to continue to maintain the DOE Coal Fired Flow Facility and keep it in readiness for anticipated testing. This effort was terminated in September 1998 by DOE stop-work letter. Work continued on reporting, environmental restoration and on the High Temperature Superconductivity work that was underway.

The work included preparing reports on the MHD POC tests that had been completed just prior to this contract initiation under an earlier contract with DOE Chicago. These four reports are summarized herein.

This report summarizes the environmental restoration work performed under the contract, including groundwater monitoring and remediation, removal of wastes from the facility, removal of asbestos from the cooling tower and actions in compliance with the license to discharge water into Woods Reservoir.

This report covers work in support of the DOE High Temperature Superconductivity program including:

- Assistance to DOE in preparing a development plan
- Cooperation with industry, national laboratories and other universities to promote the commercialization of thin film superconductors (coated conductors).
- Process Evaluations
- Process Diagnostic Development
- Process Economics

The assistance to DOE task included convening an advisory board composed of all the major participants in the DOE program and preparing a draft development plan and Research and Development Roadmap leading to commercialization of the coated conductor technology.

Under this program, cooperative agreements and cooperative work was undertaken with Oak Ridge National Laboratory, Midwest Superconductivity, Inc., EURUS Technologies, Inc., Westinghouse Electric Company, and others.

In the process evaluation task, four studies were completed by faculty, staff and students. Summaries of these studies are included in this report. In process diagnostic development, three studies were completed, all emphasizing diagnostics that are applicable to real time control of manufacturing processes. In Process Economics, one study was completed that estimated the manufacturing cost of superconducting wire produced by two of the process thought to be most promising.

1.0 General

This is the final technical report for work performed by the University of Tennessee Space Institute under Department of the Energy Contract No. DE-AC22-95PC95231. It is submitted in accordance with paragraph 4, of Part III, Section J, Attachment B, of this contract.

2.0 Scope

The scope of the report covers the following:

- Completion of reports on the POC testing that was performed under the previous DOE Contract, DE-AC02-79ET10815.

- Site environmental compliance and remediation.

- Work for others under Task 6. The only program authorized under this task was the High Temperature Superconductor work.

3.0 Work Completed

3.1 Completion of the MHD POC Program

3.1.1 Superheater/Intermediate Temperature Air Heater Tube Corrosion Test in the MHD Coal Fired Facility (Montana Rosebud Coal). The results of this effort are documented in Topical Report DOE/ET/10815-232.dated January 1996[1].

ABSTRACT

Nineteen alloy were exposed for approximately 1000 test hours as candidate superheater and intermediate temperature air heater tubes in a U.S. DOE facility dedicated to demonstrating Proof of Concept for the bottoming cycle or heat and seed recovery portion of coal fired Magnetohydrodynamics (MHD) electrical power generating plants. Corrosion data were obtained from a test series utilizing a western United States sub-bituminous coal, Montana Rosebud. The test alloys included a broad range of compositions ranging from carbon steel to austenitic stainless steels to high chromium nickel-base alloys. The tubes, coated with K_2SO_4 containing deposits, developed principally oxide scales by an oxidation/sulfidation mechanism. In addition to being generally porous, these scales were frequently spalled and/or non-compact due to a dispersed form of outward growth by oxide precipitation in the adjacent deposit. Austenitic alloys generally had internal penetration as transgranular and/or intergranular oxides and sulfides. While only two of the alloys had damage visible without magnification as a result of the relatively short exposure, there was some concern about long-term corrosion performance owing to the relatively poor quality scales formed. Comparison of data from these tests to those from a prior series of tests with Illinois # 6,

a high sulfur bituminous coal, showed less corrosion in the resent test series with the lowest sulfur coal. Although K_2SO_4 was the principal corrosive agent as the supplier of sulfur, which acted to degrade alloy surface scales, tying up sulfur as K_2SO_4 prevented the occurrence of complex alkali iron trisulfates responsible for severe catastrophic corrosion in conventional power plants with certain coals and metal temperatures.

CONCLUSIONS:

Iron based and nickel-based alloys covering a broad compositional range were exposed for approximately 1000 hours to conditions simulative of fire-side superheater and intermediate temperature air heater service in MHD power generating plants burning a relatively low sulfur, high ash, and high volatile coal, Montana Rosebud. Tests were conducted in a 20 Mw_t facility with test alloys in the form of 2.29m (7.5 feet) long pendant u-shaped tubes mounted in three duct modules called test sections, located in regions of successively lower gas temperature of interest in simulating secondary superheater, reheater, primary superheater, and intermediate temperature air heater service. Steam cooling was used to maintain tube metal temperatures ranging from 644 K (700° F) to 1033 K (1400° F). Corrosion occurred beneath deposits containing approximately 35% potassium sulfate, 30% potassium carbonate and 30% flyash. After exposure, corrosion of tube samples was evaluated in terms of scale thickness and depth of internal penetration, comparison of remaining wall thickness with initial ultrasonic thickness measurements, and qualitative microscopic evaluation of scale, penetration, and deposit morphologies. Post-test evaluations were not performed on Test Section 3 tubes because of overheating during exposure. The following conclusions were made from the evaluations performed on tubes from Test Sections 1 and 2, together with application of relevant observations and conclusions from prior work:

1. Corrosion resulted from solid state interaction of tube metals and their scales with K_2SO_4 in the deposits.

2. Complex alkali trisulfates such as $K_2Fe(SO_4)_3$, responsible for potentially severe conventional coal ash corrosion, are not normally present in MHD as a result of low SO_2 and SO_3 concentrations in the flue gas.

3. Many of the corrosion characteristics in these tests were similar to those occurring in liquid phase coal ash corrosion. These included having the same corrosion precursors (K_2SO_4), the same type of scales, and same migration of iron into the deposit to produce Fe, and precipitation of iron oxide near the outer boundary of the $FeSO_4$ as a result of decreasing sulfur partial pressure and increasing oxygen partial pressure.

4. Corrosion resulted in oxide scales containing sulfur either in solution or as discrete sulfides. Sulfur penetration of the scale resulted in enhanced outward metal ion migration and production of Cr-Fe scales often having multiple layers. Much separation of these scale layers and scale fracturing occurred, augmented by

the relative large number and intensity of thermal cycling that occurred. A red phase containing iron and sulfur, assumed to be $FeSO_4$, between the scale and the deposit appeared to be a brittle phase prone to spalling and to contributing to scale spalling. This scale damage resulted in further corrosion, and this process could eventually reach a breakaway stage wherein scales would no longer be repaired due to subsurface chromium depletion and rapid attack would occur. However, cyclic conditions were far more severe in these tests than would be expected in actual service.

5. Internal penetration of most of the austenitic stainless steels occurred as a result of inward migration of oxygen and sulfur being faster than the outward migration of cations. This penetration resulted in subscale sulfides in some cases, in transgranular oxidation/sulfidation of the surface grains, and intergranular penetration to a depth of several grains, depending upon the chromium content.

6. Resistance to corrosion generally increased with increasing alloy chromium content. Alloy CR35A with 35% Cr was the most resistant of those tested.

7. Monotonically increasing corrosion with temperature was not generally observed due to the ability of high chromium alloys to produce more protective surface scales at high temperatures than at lower temperatures.

8 There was little difference in corrosion between TS1 with a gas temperature of around 1506 K (2250° F) and hard, thick deposits, and TS2, with a gas temperature of about 1200 K (1700° F) and friable deposits. There was, however, evidence of more scale spalling at the higher gas temperature.

9 There was little dependence of corrosion on angular position around the tube. Higher frontal heat flux to the tube deposits was offset by thicker, more insulating frontal deposits so that there was no consistent pattern of temperature relative to angular position.

10. The four alloys (316, 304, 253MA, and 310) tested in both the prior LMF4 test series with Illinois # 6 coal and the later LMF5 test series with Montana Rosebud coal showed considerably lower corrosion with the Montana Rosebud coal. The difference was assumed to be due to lower sulfur content in the Rosebud coal and in the tube deposits.

3.1.2 Nitrogen Oxide Emissions from Coal Fired MHD Plants. The results of this effort are documented in Topical Report DOE/PC/95231-42.

ABSTRACT

In this topical report, the nitrogen oxide emission issues from a coal fired MHD steam combined cycle power plant are summarized, both from an experimental and theoretical/calculational viewpoint. The concept of staging the coal combustion to

minimize NO_x is described. The impact of NO_x control on design choices on electrical conductivity and overall plant efficiency are described. The results of the NO_x measurements in over 3,000 hours of coal fired testing are summarized. A chemical kinetics model that was used to model the NO_x decomposition is described. Finally, optimum design choices for a low NO_x plant are discussed and it is shown that the MHD Steam Coal Fired Combined Cycle Power Plant can be designed to operate with NO_x emissions less that 22 ng/Joule (0.05 lbm/MMBTU).

CONCLUSIONS

1. The experimental program conducted by UTSI during the MHD POC program, coupled with a validated chemical kinetic calculational methodology provides the tools needed for design of MHD Steam Power plants for prescribed levels of NO_x emissions.

2. The MHD Steam Power plant can be designed for NO_x emissions of no more than 22 ng/Joule (0.05 lbm/MMBTU).

3. Design for NO_x emissions below this level will likely require catalytic reduction.

3.1.3 The High Moisture Western Coal Processing System at the UTSI-DOE Coal Fired Flow Facility. The results of this effort are documented in Topical Report DOE/PC/95231-2[3].

ABSTRACT

The Department of Energy's (DOE) Coal Fired Flow Facility (CFFF), located at the University of Tennessee Space Institute (UTSI) in Tullahoma Tennessee, was designed to collect data necessary for the development of a commercial magnetohydrodynamic (MHD) power generating system. The CFFF has an on-site coal processing system to convert raw coal to dry, finely pulverized coal suitable for dense-phase transport to the combustor. The coal processing system was designed primarily for use with Illinois # 6, eastern type, bituminous coal. However, DOE required the use of Montana Rosebud, a western, high moisture, high volatile coal as a fuel for the second series of POC tests. Switching from Illinois # 6 to Montana Rosebud coal necessitated modification of the coal pulverizing and drying systems due to a higher moisture content and volatility of the coal. A closed-loop, inerted gas system, with a condenser to control moisture build-up, was selected to process the Rosebud coal. Nitrogen was used to limit the oxygen content of the recycled gas to below 5%. Descriptions of the process control equipment and logic are presented. Data on the resulting moisture and size distribution of the processed coal are reported.

CONCLUSIONS

1. The original eastern coal system was modified to process Montana Rosebud, a western coal. The modified system was successfully operated for over 1,339 hours prior to the completion of the MHD Proof-of-Concept (POC) testing of the integrated bottoming cycle at the CFFF. All of the design conditions for the western coal system were achieved and the design goal of a standard utility coal grind (70% through 200 mesh) was nearly achieved. The final particle size distribution produced coal of 77% through 200 mesh. A minor change to the coal system, installation of a larger baghouse rotary valve, should produce the desired standard utility grind of 70% through 200 mesh. It should be noted that the coarser grind is desirable only for use with a slag rejecting combustor such as that tested at the CDIF in Montana.

2. Coal moisture during the Montana Rosebud testing remained below the design goal of 8%, resulting in stable coal flow into the combustor for extended testing periods. For the first three tests, coal moisture remained below 5 % and very few coal flow interruptions were experienced. During the reminder of the program, the coal moisture increased because of a high percentage of raw coal fines, and as a result, the number of coal line blockages also increased.

3. A new Fischer-Porter Coriolis-type mass flowmeter was evaluated and installed during the Montana Rosebud testing phase. This new single-tube coal flow meter was more accurate and reliable than the first-generation Coriolis meters used for over thirteen years at the CFFF.

4. Due to the process control automation installed, the operation of the western coal system required no additional manpower over the prior, less complex system of processing Illinois # 6 coal. The new system has the flexibility to increase production of pulverized coal and to change the desire operating temperatures and flows.

3.1.4 Proof of Concept Tests of the Magnetohydrodynamics Steam Bottoming System at the DOE Coal Fired Flow Facility. The results of this effort are documented in Final Report DOE/ET/10815-233[4].

ABSTRACT

The development of coal-fired magnetohydrodynamic (MHD) power can be viewed as consisting of two parts: the topping cycle and the bottoming cycle. The topping cycle consists of the coal combustor, MHD generator and associated components. The bottoming cycle consists of the heat recovery, steam generation, seed recovery/ regeneration, emissions control (gas and particulate), ash handling and deposition, and materials evaluation. This report concentrates on the bottoming cycle, for which much of the technology was developed at the University of Tennessee Space Institute (UTSI).

Because of the complexity of the required technology, a number of issues required investigation. Of specific concern regarding the bottoming cycle, was the design of the steam cycle components and emissions control. First, the high combustion temperatures and the use of large quantities of potassium in the MHD combustor results in a difference in the composition of the gases entering the bottoming cycle compared to conventional systems. Secondly, a major goal of the UTSI effort was to use a variety of coals in the MHD system, especially the large reserves of high-sulfur coals available in the United States.

The Department of Energy developed a "Coal-Fired MHD Preliminary Transition and Program Plan" in 1984 and followed this with an MHD program plan in 1988. One outcome of these plans was the initiation of Proof-of-concept (POC) testing.

The first POC test at the Coal-Fired Flow Facility (CFFF) located at UTSI was completed in August 1987 while burning Illinois No. 6 coal for a total of 198 hours. At the conclusion of the Illinois No. 6 POC tests, more than 2,687 hours of operation had been accumulated on the low mass flow (LMF) test train at the CFFF. After completing the POC test objectives for the Illinois coal, preparations were made to test Rosebud coal from eastern Montana.

This report describes the Rosebud coal POC program and the major equipment modifications made on the system. It also presents the results and conclusions of tests with both coals, with emphasis on differences in performance observed between the two coals.

More than 2,000 hours of POC testing were successfully accumulated while firing Illinois No. 6 coal and nearly 1,050 hours while firing Rosebud coal. Base test conditions were similar for both coals.

Significant differences in moisture, reactivity and mineral matter composition between the Illinois and Rosebud coals required equipment modifications and led to operating differences. Significant effects are summarized below.

The coal preparations system, modified to produce a dry, pulverized coal in an inert atmosphere while pulverizing the higher moisture, more reactive Rosebud coal, performed very well. It produced a satisfactory coal particle size while providing a uniform coal feed rate.

During the Illinois No. 6 tests, the seed and coal were mixed in the pulverizer. This approach worked well, but desired changes in the mixture ratio to the combustor were difficult to achieve. This was due to the long residence time and the mixing that occurred in the storage and feed tanks. The system used for the Rosebud tests, a 47% water solution of K_2CO_3 injected with No. 2 fuel oil into the combustor, worked well. This system provided more precise control and the flow rate can be adjusted instantly. This approach does reduce the combustion temperature somewhat due to the water. However, it could be adapted to feed a potassium formate solution (from a seed reprocessing plant) or molten liquid to overcome the temperature reduction.

In spite of the very high levels of oxides of nitrogen (NO_x) generated in the combustor, emissions from the combustion of both coals were controlled to levels well below New Source Performance Standards (NSPS) requirements. Levels were slightly higher for the Rosebud coal, which was attributed to the lower sulfur content (see Reference 2 for additional detail). Sulfur dioxide emissions can be eliminated for all practical purposes by operating with sufficiently high K_2/S ratios. The sulfur dioxide (SO_2) levels were generally under NSPS requirements with potassium to sulfur (K_2/S) ratios of about 1.4 and above.

Particulate emissions for the Rosebud were finer, about 0.5 μm, compared to about 0.8 μm for the Illinois coal. The baghouse effectively reduced particulate emissions to levels well below NSPS and Combustion 2000 goals, with emissions as low as 0.132 ng/J (.0003 lbm/MMBTU) and 0.264 ng/J (.0006 lbm/MMBTU) measured for Rosebud and Illinois coals, respectively. The dry ESP improved significantly after smaller diameter electrodes, recommended by our consultant, ADA, Inc., were installed. Although the dry ESP met NSPS requirements and original Combustion 2000 goals throughout the program, performance was much more consistent after the electrodes were changed. The complete wet ESP system was not evaluated until the LMF5G test, near the end of the Rosebud coal tests. It met NSPS requirements with 21% of the total flow passing through it and Tennessee regulations with nearly 100% of the gas flow. Time was not available to fully evaluate the wet ESP system, but we believe this system can meet emission regulations. Furthermore, it has a number of advantages in an MHD system using a seed reprocessing approach with a slurry/solution input.

Ash deposition was well controlled during testing of both coals, even though gas passage ways were smaller than conventional commercial systems. The coal type had a significant effect on the deposit characteristics. The Rosebud coal conditions produced a characteristic blue deposit in the superheater high temperature module (SHTM) tube banks. Although the presence of this material did not adversely affect ash deposition, future work should include a study of the formation and possible effects of this material. Also, because reactions involving solids are very slow, ash deposition should be carefully monitored during controlled conditions over long periods of continuous operation if MHD development is ever reinstated.

Corrosion resistance of metal alloys with potential application in superheaters and intermediate-temperature air heaters increased with increasing chromium content during test with both coals. During the Rosebud tests, alloys with 20-21% Cr and high chromium to nickel ratios, performed as well as or better than other alloys with higher chromium content but lower Cr/Ni ratios. Four alloys, 316, 304, 253MA and 310, tested with both coals showed considerably lower corrosion with Rosebud coal as compared to Illinois coal, which was attributed to the lower Rosebud sulfur content. However, the corrosion data should be used carefully, because of the differences in test durations.

CONCLUSIONS AND RECOMMENDATIONS

The first eleven comments are based on the specific results of the UTSI MHD program and their relation to the UTSI objectives.

1. More than 2000 hours of POC testing were successfully accumulated while firing Illinois No. 6 coal and nearly 1050 hours while firing Rosebud coal. Base test conditions were similar for both coals.

2. Significant differences in moisture, reactivity and mineral matter composition between the Illinois and Rosebud coals required equipment modifications and led to operating differences. Significant effects are summarized below.

3 The coal preparation system, modified to produce a dry, pulverized coal in an inert atmosphere while pulverizing the higher moisture, more reactive Rosebud coal performed very well. It produced a satisfactory coal particle size while providing a uniform coal feed rate.

4. During the Illinois No. 6 coal tests, the seed and coal were mixed in the pulverizer. This approach worked well, but desired changes in the mixture ratio to the combustor were difficult to achieve. This was due to the long residence time and the mixing that occurred in the storage and feed tanks. The system used for the Rosebud tests, a 47% solution of K_2CO_3 injected with No. 2 fuel oil into the combustor also worked well. This system provides more precise control and the flow rate can be adjusted instantly. This approach does reduce the combustion temperature somewhat. However, it could be adapted to feed a potassium formate solution (from a seed reprocessing plant) or molten liquid to overcome the temperature reduction.

5. The MHD upstream simulation components performed well throughout testing with both coals, including one test during which the TRW combustor segment was installed. A topping cycle diagnostic access ring was successfully installed and pressure measurements were made.

6. Excess potassium carbonate in the combustion gases (due to the lower Rosebud sulfur content) increased the secondary combustion ignition temperature compared to the Illinois coal tests. Adequate procedures were developed to compensate for these differences.

7a. The particulate emissions were slightly finer for the Rosebud coal than for the Illinois coal (about 0.5 µm or less compared to 0.8 µm, respectively).

7b. The baghouse was effective in reducing particulate emissions to levels well below NSPS and Combustion 2000 goals, with efficiencies generally above

99.9%. Levels as low as 0.0003 and 0.0006 lb/MBtu were measured at the baghouse outlet for the Rosebud and Illinois coals respectively.

7c. The dry ESP performed erratically during the POC tests with both coals. The problem was resolved after smaller diameter electrodes were installed on the recommendation of ADA, Inc. Even with erratic performance, emissions during the Illinois coal test well below NSPS requirements and original Combustion 2000 goals were achieved during some tests. After the electrodes change, emissions were consistently below NSPS goals at rated flow rates.

7d. The final component of the wet ESP system, the rotary drum filter, was not installed until the LMF5G test. It was designed to replace the wet scrubber, to take all the exhaust flow and meet permit requirements (20% capacity). The wet ESP met NSPS requirements with 21% of the total gas flow passing through it. It also met Tennessee regulations with more than 98% of the gas flow passing through it. At about design flow conditions, emissions were above NSPS but did meet the Tennessee regulations for which it was designed. Test time was not available to fully evaluate this system, but it is our belief that this system can meet emission requirements. It also has a number of advantages in a system employing a seed reprocessing approach using a solution or slurry input.

7e. An economic evaluation of the three systems evaluated is required to select the optimum cleanup device.

7f. No EPA toxic organic compounds were detected in the MHD solid emissions. Inorganic toxics were well below the allowable limits for landfilling of solids. Vapor and particulate emissions contained only trace levels of inorganic pollutants. The study showed that nearly all of the organic matrix is destroyed in the MHD system.

8. In spite of very high levels of NO_x generated in the combustor, emissions for both coals were controlled to levels well below NSPS requirements. Levels were slightly higher for the Rosebud coal, which was attributed to the lower sulfur content. Sulfur dioxide emissions can be eliminated for all practical purposes by operating with sufficiently higher K_2/S levels. The SO_2 levels were generally under NSPS requirements with a K2/S ratio of about 1.5 and above.

9. A radiometric line reversal gas temperature monitor, a non-intrusive device, was successfully developed to measure temperatures at the SHTM inlet.

10a. Ash deposition was well controlled during testing of both coals, even though gas passage ways were smaller than conventional commercial systems. The coal type had a significant effect on deposit characteristics. The Rosebud coal conditions produced a characteristic blue deposit in the SHTM tube banks. Although it did not adversely affect ash deposition, future work should include a study of the causes of this blue color. Also, because reactions involving solids are very slow, ash deposition should be carefully monitored during controlled conditions over long periods of continuous operation if MHD development is ever reinstated.

10b. A comprehensive model, considering factors lacking in other available studies, related well to experimental data. It is recommended that work continue on this model for MHD as well as for conventional boiler applications.

11. Corrosion resistance of metal alloys with potential application in superheaters and intermediate-temperature air heaters increased with increasing chromium content during tests with both coals. During the Rosebud tests, alloys with 20-21% Cr and high chromium to nickel ratios, performed as well as or better than other alloys with higher chromium content but lower Cr/Ni ratios. Four alloys, 316, 304, 253MA and 310 showed considerable lower corrosion with Rosebud coal than with Illinois coal, which was attributed to the lower Rosebud sulfur content. However, the data should be used carefully because of the differences in test durations. Additional data must be required to provide design information for commercial plants. Information must also be acquired to develop design data and evaluate performance of materials (metallic & ceramic) for application in the primary furnace reducing zone.

3.2 Environmental Restoration of the DOE Coal Fired Flow Facility

3.2.1 Carrying out the State of Tennessee Groundwater Remediation Plan

The work under this subtask required drilling wells, sampling and analysis of groundwater in locations around the CFFF site. Residual diesel levels were found in the samples from wells around the 10,000 gallon diesel tank, which had experienced two known spills during the test program. This was remediated by digging up surface contaminated soil around the tank and ultimately disposing of it in an approved landfill.

Two of the wells continue to show organic materials above standards and the State of Tennessee has directed additional remediation measures that are still in progress.

3.2.2 Disposal of Industrial Type Non-Hazardous Waste

This subtask involved disposal of non-hazardous wastes such as water treatment chemicals, raw coal, small amounts of pulverized coal and ash and spent seed (potassium carbonate and potassium sulfate) accumulated from test programs. With the exception of approximately 200 tons of raw Montana Rosebud coal, these materials have been disposed of. The raw coal disposition is still under consideration. A local coal company will take it but will require UTSI to pay for transportation to their site, where it will be blended with other coal and burned. The alternative is to pay to haul it to a landfill and pay to dispose of it.

3.2.3 Disposal of Asbestos Containing Material in CFFF Cooling Tower

The asbestos has been removed from the CFFF cooling tower and properly disposed of by a qualified contractor. This was done in connection with a major renovation of the cooling tower in preparation for tests under a different DOE program, the Foster Wheeler managed High Performance Power System (HIPPS) program.

3.2.4 Carrying out the Responsibilities under the State of Tennessee Water Discharge Permit

This subtask included the management of the CFFF holding ponds and the sampling and analysis of any discharge from them to Woods Reservoir. This program has been completed and no further actions are required.

3.3 High Temperature Superconductivity Program

3.3.1 Program Planning Assistance to DOE

Under this subtask, UTSI was directed to perform two tasks:

- In coordination with major participants, develop a draft national plan for "Development of Manufacturing Processes for Practical Coated Conductors used in High Field Magnets". This was later renamed "Research and Development Roadmap to Achieve Electrical Wire Advancements from Superconducting Coatings". In furtherance of this mission, a Coated Conductor Development Steering Committee was formed that had members from most of the organizations working in this field. With the assistance of this group, a draft plan was prepared and submitted to Energetics, Inc., a DOE headquarters support contractor, to finalize it and publish as a DOE Development Plan. In addition, UTSI issued a subcontract to Energetics, Inc. to cover this work and other DOE support work.

- UTSI was tasked to work with commercial companies, national laboratories and others involved in the development of coated conductors to foster the development and commercialization of the technology. In support of this objective the following alliances were formed:

  a) Two graduate students were assigned to work at ORNL to perform research tasks.

  b) A laboratory program was undertaken in support of Midwest Superconductivity, Inc., to identify methods to assure the quality of raw chemicals (barium, yttrium and copper THD compounds) used in their MOCVD process that they hoped to commercialize.

c) An x-ray diffraction system was purchased and installed and used to support process development by EURUS Technologies, Inc., Westinghouse Electric Corporation, Midwest Superconductivity, Inc., and ORNL.

d) A cooperative agreement was made with EURUS Technologies, Inc., to cooperate in optimizing rolled nickel substrate. Under this agreement UTSI performed the annealing, x-ray diffraction analysis, provided SEM and other laboratory support. EURUS rolled the nickel samples and applied YBCO films on some UTSI annealed samples.

e) Joined a consortium to develop solution based manufacturing processes. The team members were EURUS Technologies, Inc., Sandia National Laboratory, Clemson University, The University of Houston, and the National Magnet Laboratory.

3.3.2 Process Evaluations

3.3.2.1 Bench Scale Evaluation of Solution-Growth based Techniques for Manufacturing HTS wire/tape. The results of this effort are documented in Topical Report, DOE/PC/95231-18[5].

ABSTRACT

High Temperature Superconductors (HTS) offer significant potential cost savings because of their negligible resistance to the flow of electric current. Several methods exist to fabricate HTS wire and other HTS products. The University of Tennessee Space Institute (UTSI) carried out an evaluation of the state-of-the-art methods. Based on the conclusions of the report, it was decided to focus on the solution-growth based methods to prepare the buffer layer(s) and the superconductor layer. In most of the studies spin-coating is used for fabricating these thin films. However, for manufacturing long lengths of HTS wire dip-coating is an easy method to scale-up. Hence the study of fabricating such thin films by dip-coating is required.

In this work, a dip-coating unit to coat substrates was assembled. Spin-coating was used to coat when the solution was very viscous as in the case of the metal organic decomposition (MOD) route. The epitaxial growth of lanthanum aluminate (buffer layer) on single crystal substrates and textured substrates, and yttrium barium copper oxide (HTS) on single crystal substrates was studied. In particular, the effect of major process parameters on some of these systems is reported in this report. For the superconducting

films, transport property measurements were carried out. Based on the conclusions of this study recommendations are made for further studies.

RECOMMENDATIONS

Following the solution growth techniques the epitaxial growth of LAO was achieved for LAO on STO (100) single crystal substrates and also for YBCO on LAO(100) and STO(100) single crystal substrates. Hence the next step is to combine the two ideas and grow YBCO on LAO/STO films formed by the sol-gel method. A high critical current density (J_c) was achieved on one sample of superconducting YBCO film grown on single crystal substrate of LAO. If one is able to achieve a similar or higher value of J_c on YBCO films grown on the substrate with a buffer layer, it should show a good prospect for YBCO films grown on textured nickel substrates with a buffer layer. Once J_cs of the order of 1 MA/cm^2 are achieved on the LAO/STO films, the following step should be to achieve this target for similar films grown on the LAO/Ni films. A variety of options exist in optimizing the final properties of the superconducting tape. These include starting out with different precursors that have higher solubilities in the same solvent, and optimizing the time-temperature and atmosphere program for processing the samples.

Although it was planned to carry out some experiments based on the following approach, constraints of time and optimum results (i.e. best results on single crystal substrates) proved to be obstacles. Buffer layers and superconductor films are grown by several methods. It is not necessary that if the buffer layer is grown by one technique, that the superconductor also needs to be grown by the same. A combination of different techniques may prove to be a viable option. Some of the combinations possible are:

1. YBCO grown by MOD method on a buffer layer which is grown on textured nickel by some of the state-of-the art technique. The techniques to grow buffer layers and superconductors are constantly evolving and hence the best-suited option should be explored.

2. YBCO grown on LAO(grown by sol-gel)/Ni (RABiTS). The YBCO can be grown by any technique that has proven successful on single crystal or other substrates. The BaF_2 process, which uses e-beam for making YBCO films at ORNL, is one such technique.

The coated sample lengths generally were around 8 mm for the single crystal substrates and 8 - 15 mm for textured nickel. The advantages of making a sample of long length (> 2 mm) are two-fold:

1. The area with uniform coating would increase because of the reduction in the percentage of the unevenly coated ends and therefore the end effects.

2. Long length samples with high critical current density would enhance industrial interest in the solution based growth techniques.

Hence the dip-coating unit needs to be modified to enable coating long length samples.

3.3.2.2 Evaluation of Methods for Application of Epitaxial Buffer and Superconductor Layers. Documented in Topical Report DOE/PC/95231-11[6]

ABSTRACT

The recent achievements in a number of laboratories of critical currents in excess of 10^6 a/cm^2 in YBCO deposited over suitably textured buffer/substrate composites have stimulated interest in the potential applications of coated conductors at high temperatures and high magnetic fields. As of today, two different approaches for obtaining the textured substrates have been identified. These are: Los Alamos National Laboratory's (LANL) ion-beam assisted deposition called IBAD, to obtain a highly textured yttria-stabilized zirconia (YSZ) buffer on nickel alloy strips, and Oak Ridge National Laboratory's (ORNL) rolling assisted, bi-axially textured substrate option called RABITS.

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

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

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

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

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

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

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

- Process Flow Schemes and Involved Operations
- Multi-Attribute Analysis Carried out for Objective and Subjective Criteria
- Manufacturing Parameters to Process 6,000 km/yr of Quality Coated Conductor Material
- Metal Organics Decomposition (MOD), Sol-Gel, MOCVD, E-beam and PLD as the Leading Candidates and Technical Concerns/Issues that Need to be Resolved to Develop a Commercially Viable Option Out of Each of Them.

This report also includes generic areas in which additional research and development work is 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.

CONCLUSIONS AND RECOMMENDATIONS

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

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

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

- Cost of Chemicals—

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

- Mass transfer and reaction kinetics data—

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

- Diagnostics and control—

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

- Environmental issues—

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

- Outer passivation/insulation layer—

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

- Splice connections—

  It seems that in commercial manufacturing of long-length coated conductors, a significant fraction of the production may not meet the product specifications. As a result, need may exist to connect sections of the good/acceptable wires to make a long wire of the 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 or the cost of producing long-length conductors can escalate significantly.

- Overall cost of production—

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

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

3.3.2.3 Experimental Study of the Effects of Annealing Time, Equilibrium, Angle, and Absolute Misorientation Angle on Thermal Grain Boundary Grooving in Cube-Textured Nickel. Documented in DOE/PC/95231-27[7].

ABSTRACT

Several technical problems are associated with the rolling-assisted biaxially textured substrates (RABiTS) method of fabricating long lengths of high temperature superconducting wire. For example, controlling or eliminating thermal grain boundary

groove defects on the Ni base layer of the substrate is an important concern. Thermal grooves on the surface of the Ni may have the potential to cause cracks or growth defects to form in the buffer and superconducting layers which are epitaxially deposited on the Ni. Thus, the effects of annealing time, equilibrium angle and absolute misorientation angle on thermal grain boundary grooving in cube-textured nickel were investigated.

Small samples of RABiTS Ni were recrystallized at 800°C for times of 10, 30, 60 and 120 minutes to produce diffusion-induced thermal grooves on their surfaces. The linear dimensions and equilibrium angles of these grooves were measured using atomic force microscopy. The misorientations of grains at triple point junctions were measured using electron backscatter diffraction, and the cube-texture of the samples was analyzed with x-ray diffraction. Grain size measurements were also made on each sample.

Linear dimensions of grooves evolved with annealing time in accordance with Mullins' theory of thermal grooving. Average groove depths increased with increasing equilibrium angle; however, there was only a slight tendency for groove depth to increase with increasing absolute misorientation angle. In general, groove depths did not exceed 650 Å. The cube texture and grain size of the samples were typical of RABiTS Ni.

CONCLUSIONS

The effects of annealing time, equilibrium angle and absolute misorientation angle on thermal grain-boundary grooving in cube-textured nickel have been investigated. This study has revealed that Mullins theory adequately describes the thermal grooving phenomenon in RABiTS nickel. Thus, his theory may be used to predict the time dependent growth behavior of thermal grooves. Also, Mullins' theory shows how the equilibrium angle of a groove can affect its growth. Concerning absolute misorientation angle, its effect on grooving is difficult to determine because of other factors that affect the grain-boundary energy. The specific conclusions developed from this work are as follows:

1. Thermal grain-boundary grooves form in abundance on RABiTS Ni samples annealed at or above 800°C. These grooves can occur in two morphologies: diffusion-induced and faceted. The groove morphology depends on the conditions of annealing, specifically the annealing temperature and the local annealing atmosphere.

2. On average, the dimensions of diffusion-induced, thermal grain-boundary grooves on RABiTS Ni samples increase with time in accordance with Mullins' theory of groove formation and growth by surface diffusion. Thus, the initial growth rate of thermal grooves is very rapid with the rate decreasing with increasing annealing time.

3. Generally, the thermal grooves in RABiTS Ni have very small dimensions with depths no larger than 650Å and widths no larger than 2.5 µm after 2 hours of

annealing at 800°C in vacuum. However, some deep grooves (≤ 1500 Å) were observed surrounding small grains (10-20 μm).

4. From AFM measurements, it was determined that the average depth of thermal grain-boundary grooves increases with increasing equilibrium angle in the small-slope regime. Equilibrium angle has no measurable effect on groove width.

5. A strong relationship does not exist between absolute misorientation angle and grain-boundary groove depth; however, there seems to be a tendency for groove depth to increase with increasing misorientation angle. The lack of a strong correlation may be due to the effect of grain-boundary plane orientation on grain boundary energy.

6. The grain size and degree of cube texture of the RABiTS Ni samples examined in this experiment are consistent with results reported previously by Goyal of ORNL.

7. Although grain-boundary grooves in RABiTS Ni were observed to have a high ratio of width to depth (30:1) and do not appear to be a serious mechanical flaw, they may still cause growth defects to form in subsequently deposited layers of a RABiTS substrate. These growth defects could create mechanical weaknesses in the oxide layers that may rupture under stress.

8. Using the data collected in this study, more research is necessary to determine if grain-boundary grooves in RABiTS Ni can behave as initiation sites for cracks in the oxide layers (buffer and superconductor) under specific types of mechanical loading.

9. Because thermal grooves are formed as a result of a surface effect, it may be possible to stop their formation by altering the surface condition of the material. For example, the Ni could be recrystallized at low temperature to form the cube-texture. At 400-500°C, no significant grooves would form. Then the sample could be coated with an oxide buffer layer and annealed at high temperature to bring grain growth to an effective termination. This final anneal would also refine the cube-texture.

As mentioned previously, grain-boundary grooves do not seem to be severe mechanical defects because of their subtle geometry, but they should not be dismissed because other serious flaws may form as a result of their presence. The information presented in this report is intended to provide a basis for further work in which the effects of thermal grooves on the performance of layered conductors are modeled or experimentally determined.

3.3.2.4 Statistically Designed Experimental Study of Sol-Gel Based Film Coating Scheme for High Temperature Superconductors and Buffer materials and Related Manufacturing Process Cost Evaluation. Documented in Thesis Report DOE/PC/95231-29[8].

ABSTRACT

In this work, processing factors that influence the epitaxial growth of $LaAlO_3$ on cubic-textured nickel substrates via sol-gel route were investigated using a Taguchi L12 experimental design. Through experimental data collected on omega FWHM, phi FWHM, and composition of orientations, a set of models was generated to characterize the epitaxial growth response to various processing factors. These factors included thermal processing time, temperature, atmosphere, nickel surface roughness, degree of precursor hydrolysis, withdrawl rate, and precursor solution concentration. Based on the results, appropriate processing conditions were then identified to produce the greatest degree of epitaxial growth as defined by the nondimensional term.

Also, this work explored the manufacturing aspects of the sol-gel based film coating scheme through a preliminary costing study. Production objectives were kept the same as the ones used in the similar cost studies carried out for other schemes based on methods such as evaporative electron beam, pulsed laser deposition, and metal organic chemical vapor deposition. Also, the final product cost was compared to an industrial goal established by DOE and sensitivity of assumptions made in the study were examined in regards to meeting this goal.

CONCLUSIONS

The effects of several processing parameters on the epitaxial growth of $LaAlO_3$ on cube-textured nickel were successfully evaluated using Taguchi L12 screening experiments. The epitaxial growth was performed without annealing of the nickel substrate before coating. The characterization involved the development of a non-dimensional term, epitaxial #, to weigh together the in-plane and out-plane sharpness along with the composition of each crystal orientation. This characterization also involved the successful development of variance and response models that could be used to identify the trends in the epitaxial # and to differentiate significant factors from the insignificant ones. These models were developed on the basis of each experiment's phi, omega and phase scan results and then separately based on the combined performance number (epitaxial #). The results were used to confirm the existence of trends in the responses and to identify the possible reasons for them.

The experimental results suggested that the major factors in determining the epitaxial growth were the oven temperature, solution concentration, oven time, and oven atmosphere. Increasing the oven time and temperature while decreasing solution concentration and maintaining 4% hydrogen in argon provided higher epitaxial #'s. Eight confirmation runs were used to validate the observed trends. Results from these confirmation runs showed marked improvement in all aspects (phi FWHM, omega FWHM, phase ratio). Also, the phase scans showed the presence of one dominant peak of $LaAlO_3$ (100). The average FWHM of omega and phi were 11.94° and 12.31°, respectively. These were comparable to the omega and phi FWHM average values of 10.55° and 15.75° reported by Vineet Lasrado who used ORNL supplied RABiTS nickel that had been annealed prior to dip-coating (Lasdrado 1998). In-plane twins were also found at half the intensity as the (100) oriented $LaAlO_3$. The presence of such twins was also reported in the work done by Lasrado.

The processing parameters that produced the improved results were as follows:

Oven Temperature =1150°C Oven Time = 1 hr
Oven Atmosphere = 4% H_2 in Ar Solution Concentration = 0.10 M
Withdrawl Velocity = 3 cm / min Degree of Hydrolysis = 1.3
Surface Roughness = 0 (Electropolished State)

Samples that were electropolished prior to coating also showed an identifiable trend of improved Epitaxial growth. Optical profilometer scans of the surface roughness of polished and unpolished scans were, however, inconclusive and did not show any improvement in the surface roughness with electropolishing. Instead, the improved results seemed to be linked to the etching away of possible surface contaminants during the electropolishing process. Optical profilometery measurements also indicated that the surface roughness increased between the unannealed and annealed cube-textured nickel samples. Ra values increased from 0.43 to 0.98 microns with annealing times of twenty hours or more. This may be explained in terms of the thermal grain boundary grooves forming and enlarging during the annealing step.

Finally, the use of an intermediate cube-textured NiO layer was also explored for the possibility of processing in air and improving the film texture. The results indicated it provided neither. At temperatures above 1050°C, the NiO layers broke down. In air, the NiO peaks grew as shown by the phase scan, but the $LaAlO_3$ peaks disappeared. Some phase scans also indicated an enlarging of the lattice parameters, suggesting a possible cross-contamination between $LaAlO_3$ and NiO.

3.3.3 Process Diagnostic Development

3.3.3.1 An Evaluation of Absorption Spectroscopy to Monitor $YBa_2Cu_3O_{7-x}$ Precursors for Metal Organics Chemical Vapor Deposition Processing. Documented in Topical Report DOE/PC/95231-23[9]

ABSTRACT

Absorption spectroscopy was evaluated as a technique to monitor the metal organics chemical vapor deposition (MOCVD) process for forming $YBa_2Cu_3O_{7-x}$ superconducting coated conductors.

Specifically, this study analyzed the feasibility of using absorption spectroscopy to monitor the MOCVD supply vapor concentrations of the organic ligand 2,2,6,6-tetramethyl-3,5-heptanedionate (TMHD) metal chelates of barium, copper, and yttrium. $Ba(TMHD)_2$, $Cu(TMHD)_2$, and $Y(TMHD)_3$ compounds have successfully been vaporized in the MOCVD processing technique to form high temperature superconducting "coated conductors," a promising technology for wire fabrication.

The absorption study of the barium, copper, and yttrium (TMHD) precursors was conducted in the ultraviolet wavelength region from 200nm to 400nm. To simulate the MOCVD precursor flows the $Ba(TMHD)_2$, $Cu(TMHD)_2$, and $Y(TMHD)_3$ complexes were vaporized at vacuum pressures of 0.03-10 Torr. Spectral absorption scans of each precursor were conducted to examine potential measurement wavelengths for determining vapor concentrations of each precursor via Beer's law.

The experimental results show that under vacuum conditions the barium, copper, and yttrium (TMHD) precursors begin to vaporize between 90°C and 135°C, which are considerably lower vaporization temperatures than atmospheric thermal gravimetric analyses indicate. Additionally, complete vaporization of the copper and yttrium (TMHD) precursors occurred during rapid heating at temperatures between 145°C and 195°C and after heating at constant temperatures between 90°C and 125°C for approximately one hour, whereas the $Ba(TMHD)_2$ precursor did not completely vaporize. At constant temperatures, near constant vaporization levels for each precursor were observed for extended periods of time. Detailed spectroscopic scans at stable vaporization conditions were conducted.

CONCLUSIONS AND RECOMMENDATIONS

Experimental results from this research effort indicate that absorption spectroscopy is a feasible diagnostic for monitoring the YBCO precursor vapor concentrations during MOCVD processing. The results show that absorption spectroscopy yields high sensitivity, which enables the monitoring of the vapor concentrations of very small concentrations of the Cu, Y, and Ba MOCVD precursors. Results of the absorption experiments indicate that prolonged monitoring of precursor vapor concentrations is attainable. Additionally, the experimental results provide critical information relevant to temperature ranges at which the precursors experience initial vaporization under MOCVD vacuum conditions. All of the (TMHD) precursors analyzed showed that stable absorption levels were observable for extended periods of time (1-2 hours). The results of the $Cu(TMHD)_2$, $Y(TMHD)_3$, and $Ba(TMHD)_2$ experiments show that these precursors begin to vaporize between 90°C and 135°C, temperatures considerably lower than atmospheric thermogravimetric analysis indicates. Additionally, the $Cu(TMHD)_2$ and $Y(TMHD)_3$ precursors are completely vaporized after heating periods of about one hour at temperatures of 90°C to 125°C. The $Ba(TMHD)_2$ experiments indicate that this precursor experiences about 50% vaporization after extended heating periods of temperatures between 100°C and 300°C.

The results of the $Cu(TMHD)_2$ absorption analyses indicate that this precursor begins changing to the vapor state in the 90-95°C temperature range and is completely vaporized between 145°C and 155°C using rapid heating. Stable absorption conditions for extended periods of time, one to two hours, permitted detailed absorption scans. All absorption experiments involving the $Cu(TMHD)_2$ precursor resulted in total vaporization of the sample in a less than 1Torr vacuum after about an hour at a constant temperature of 90-95°C. Additionally, the absorbance peak wavelengths are in good agreement with the reference absorbance peak wavelengths for $Cu(TMHD)_2$ dissolved in hexane.

The results of the $Y(TMHD)_3$ absorption analyses show that this precursor in a vacuum experiences initial vaporization in the 110-120°C temperature interval and is completely vaporized between 185°C and 195°C using rapid heating. Stable absorption conditions for extended periods of time were also attainable for this precursor. Similar to the $Cu(TMHD)_2$ samples, all of the absorption experiments involving the $Y(TMHD)_3$ precursor in a less than 5Torr vacuum resulted in total vaporization of the sample after about an hour at constant temperatures as low as 120-125°C. Likewise, the absorbance peak wavelength identified is identical to the reference absorbance peak wavelength.

Results of the $Ba(TMHD)_2$ absorption tests indicate that this precursor at vacuum experiences initial vaporization in the 125-135°C temperature range. However, all absorption analyses involving this precursor reveal that it only partially vaporizes at temperatures up to 300°C. Approximately 50% of the $Ba(TMHD)_2$ precursor pre-heat mass was vaporized. A large absorption peak in the 200-250 nm region is not present in the reference $Ba(TMHD)_2$ scans. This could be due to differences in the precursor materials used in the experimentation or the samples themselves being contaminated before this research effort was conducted.

Recommendations pertaining to the design and development of in-situ absorption spectroscopy diagnostics to monitor YBCO fabrication by MOCVD are a result of this research effort. The 50.8cm path length of the absorption chamber resulted in high absorption of the precursor samples. Since these precursor materials are so absorptive in the UV wavelength region, it is clear that the method would be very sensitive and needs a short path length.

Appropriate future work on this research effort includes covering other wavelength intervals. Also, utilizing better optical mounting arrangements would eliminate the constant alignment requirements. The analysis of precursor samples produced by different manufacturers would allow a more thorough investigation of the precursor vapor properties, particularly for $Ba(TMHD)_2$. Further absorption experiments with the $Ba(TMHD)_2$ precursor in the 200-250 nm wavelength region are needed to determine the validity of the observed 200-250 nm peak. Scans of a different $Ba(TMHD)_2$ sample are particularly recommended. Likewise, conducting absorption analyses of a mixed sample composed of all three precursors would determine if the absorption spectra of the precursors are distinguishable. This would allow evaluation of absorption spectroscopy as a monitor of MOCVD chamber concentrations of all three precursors simultaneously.

Finally, more accurate concentration measurements are needed so accurate molar absorptivities can be determined.

3.3.3.2 Characterization of High Temperature Superconductor Film Layers Using Raman Spectroscopy. Documented in Topical report DOE/PC/95231-24[10].

High Temperature superconductor films can be characterized using Raman spectroscopy to obtain the crystal orientation, oxygen concentration, and layer thickness for the film layers. This information is essential in determining characteristics of the films, such as transition temperature and current density. Good quality films need high transition temperature and current density.

Previously published work shows that the theory and background work on Raman spectroscopy on high-temperature superconductor films gives this information. Earlier research on high-temperature superconductor films shows how the films can be characterized. By applying these different methods Raman data can be used as an effective analytical technique.

An experimental setup was designed to evaluate the feasibility of acquiring the data quickly in an industrial environment using alternate technology than that used by previous researchers. Previous work in this area has been restricted to microprobe techniques that study single crystals of the superconductor. A technique is used which could give overall Raman data from a large area of the film, as opposed to single crystals or grains.

Background and experimental work described in this report include a method for determining layer thickness in buffer and superconducting film layers. Data is collected from a single film sample and a proposed buffer layer sample. This data is used to identify necessary improvements to the basic experimental setup to create a real-time, in-situ, Raman diagnostic setup for use in industrial, high-temperature superconductor film processes.

CONCLUSIONS

The need for in-situ diagnostics in the manufacture of HTSC films can be met with a Raman spectroscopy technique. Previous work concerning YBCO films documents the large amount of information that can be obtained using Raman spectroscopy. Information on oxygen concentration, crystal orientation, and layer thickness can be determined.

Raman spectroscopy not only supplies information about the YBCO layer, but also about any of the buffer layers or the substrate. Techniques similar to those used for the YBCO layer could also be used for any of these other layers. This report presents a method for determining layer thickness of YBCO layers. This method could be adapted to determine the thickness of buffer layers, such as $LaA1O_3$.

The Raman spectroscopy techniques, as described in this report, would have to be adapted to acquire the needed data for in-situ diagnostics. Such a technique could use a laser diode to irradiate the film. The light could be detected by two photodiodes, each utilizing filters to pick out certain Raman lines. For example, by detecting the 500 and 335 cm^{-1} lines the degree of c-axis tilt of the YBCO film could be found. Such a technique could also be used to determine layer thickness in any of the other layers by using the proper Raman lines.

More research and improvements to the experimental setup must be done before specific industrial applications are determined. The setup must be adapted to acquire data within the time constraints of an industrial setting. By using the methods outlined in this report, for increasing Raman signals and signal-to-noise ratios, a Raman technique should be able to be designed for online, real time data acquisition. Raman spectroscopy research shows promise as a possible diagnostic technique for the in-situ monitoring of film layer quality

3.3.3.3 Development of *IN-SITU* Control Diagnostics for Application of Epitaxial Superconductor and Buffer Layers. The results of this Effort are documented in Topical Report DOE/PC/95231-24[11].

ABSTRACT

The recent achievements of critical currents in excess of $1x10^6$ amp/cm^2 at 77K in YBCO deposited over suitably textured buffer/substrate composites have stimulated interest in the potential fabrication of these “coated conductors” as “wire”. Numerous approaches and manufacturing schemes for producing coated conductor wire are currently being developed. Recently, under the U. S. Department of Energy (DOE’s) sponsorship, the University of Tennessee Space Institute (UTSI) performed an extensive evaluation of leading coated conductor processing options. 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 evaluation to define the most viable options for a commercial fabrication process. All fabrication processes will need process control measurements. This report provides a specific review of the needs and available technologies for process control for many of the coated conductor processing options. This report also addresses generic process monitoring areas in which additional research and development are needed. The concentration is on the two different approaches for obtaining the textured substrates that have been identified as viable candidates. These are the Los Alamos National Laboratory’s (LANL) ion-beam assisted deposition, called IBAD, to obtain a highly textured yttria-stabilized zirconia (YSZ) buffer on nickel alloy strips, and Oak Ridge National Laboratory’s (ORNL) rolling assisted, bi-axially textured substrate option called RABiTS™.

CONCLUSIONS

The major issues for economical manufacturing of long-length YBCO-coated conductors pertain to developing a capability of continuously and uniformly depositing substrates, conductor and inerting layer coatings with correct orientation at high rates over a large area. Of course such a capability for the conductor has to meet the very important YBCO requirements of proper stoichiometric composition and epitaxial crystalline structure. For each of the potential coating methods examined, very sophisticated and quick response type diagnostics and control system will be needed to maintain a high J_c performance throughout the entire length of the conductor. On-line control systems to meet such needs are often not sufficiently developed or do not exist. Experiences from the related commercial operations, such as semiconductor fabrication, can be useful but the needs may be quite different. Therefore, parameters of importance and ways and means to monitor them on-line may need significant development efforts. That effort is on going, in selected critical areas. Some measurement needs can use diagnostics employed in making small sample (and sometimes single crystal) conductors, but usually those diagnostics require further development to decrease evaluation time and allow rapid on-line, real time measurements.

3.3.3.4 Evaluation of Ellipsometric Monitors for Process Control of High Temperature Superconductors. Documented in University of Tennessee M. S. Thesis of K. Peterson[12].

ABSTRACT

As various manufacturing processes are being developed, it has become clear that diagnostics and control are essential for producing high quality HTSCs. The YBCO superconductors are biaxial crystals that yield high critical current densities only if the individual crystals exhibit a high degree of alignment in the c-axis. Hence care must be taken in the manufacturing processes to ensure good alignment of the YBCO crystals. It has also been shown that the thickness of individual layers of a superconducting film stack affects the quality of the superconductor. Therefore, in order to produce high quality superconductors, it is also required that the film thickness of each layer in a film stack be monitored throughout the manufacturing process.

A brief review of several methods of on-line, real time measurement of layer thickness was performed. Based on this comparison, the ellipsometry method was chosen as the most promising, especially for application in a manufacturing environment. Several computer simulations were conducted to investigate the performance of ellipsometric methods. Since angle of incidence error is a primary source of error in a process control environment, the primary focus of the simulations was to examine the effects of angle of incidence error on ellipsometric measurements.

CONCLUSIONS

Several methods of monitoring film thickness have been presented. Interferometric methods are not well suited for process control of HTSC thin films because of stable setup requirements, the inability to measure absorbing films, and significant error induced by surface roughness. While the method of picosecond ultrasonics may be a suitable method, it is expensive compared to other methods and currently more suited for opaque films.

Photometric ellipsometric methods are the recommended choice for thickness measurements on superconducting film stacks for a variety of reasons. Measurements are fast, nondestructive, accurate and are relatively insensitive to surface roughness compared to other methods. If surface roughness is significant, it can be modeled by using ellipsometric techniques. The types of thin films and various configurations of a thin film stack that can be characterized by ellipsometric methods are not as limited as with other methods. Ellipsometric methods are also the most sensitive techniques for thickness determination in very thin films (< 30Å). It should also be pointed out that Ellipsometric methods have the advantage of measuring two independent parameters, whereas reflectance techniques measure just one. Reflectance methods are power measurements while ellipsometric measurements are intensity independent. This makes ellipsometric techniques inherently more powerful in determining optical parameters of a thin film.

3.3.4 Process Economics

Life Cycle Cost Study for Coated Conductor Manufacture by Electron Beam and Pulsed Laser Deposition Systems". Documented in DOE/PC/95231-16.

ABSTRACT

This report postulates conceptual designs for two manufacturing processes for producing thin film (coated conductor) YBCO superconductor wire. The processes considered are the electron beam and the pulsed laser deposition processes. For each system a capital cost estimate is presented for a plant to manufacture 18,000,000 meters per year. In addition, cost of operation of the plant, including staffing labor, maintenance, and consumables is included so that a cost of manufacturing of the wire can be computed based on a life cycle cost estimating procedure. The cost of wire produced is calculated for two achieved current densities, 10^6 and 10^5 amperes/cm^2 .

To evaluate the assumptions made in the calculation, sensitivity analyses are included for deposition rate, capacity factor, plant lifetime, critical current density achieved, material utilization rate, thickness of the YBCO layer, thickness of the required buffer layer, operating temperature and laser energy target removal efficiency.

CONCLUSIONS

The results of this study establish a framework for evaluation of the cost impact of many performance parameters in coated conductor manufacturing systems. Since the cost and concepts are based on early developmental results and engineering judgment, the study should be updated periodically based on latest data to enhance its usefulness. The study should be expanded to include other promising processes under consideration or development for manufacture of coated conductors. Review of this study by as wide a group of experts from industry, national laboratories and universities as possible is desirable to facilitate improving accuracy of the estimates and communication on the issues involved.

The results for the case of achieving the $10/kA-m goal at a J_c of 10^5 a/ cm^2 applicable to applications requiring a magnetic field perpendicular to the direction of current flow may be viewed as somewhat discouraging. However, there is ample margin for improvement due to continued development and engineering that could enable meeting the goal of $10/kA-m.

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