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**CRADA Final Report
for
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**ADVANCED HIGH TEMPERATURE
SUPERCONDUCTOR
FILM-BASED PROCESS USING RABiTS**

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**Prepared by the
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Oak Ridge, Tennessee 37831
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ADVANCED HIGH TEMPERATURE SUPERCONDUCTOR FILM-BASED PROCESS USING RABITS

A. Goyal, R. A. Hawsey, J. Hack, and D. Moon

ABSTRACT

The purpose of this Cooperative Research and Development Agreement (CRADA) between Lockheed Martin Energy Research Corporation (Contractor), Managing contractor for Oak Ridge National Laboratory (ORNL) and Midwest Superconductivity, Inc. (MSI) and Westinghouse Science & Electric Company (WEC) was to develop the basis for a commercial process for the manufacturing of superconducting tape based on the RABiTS technology developed at ORNL. The chosen method for deposition of YBCO films on RABiTS was Metal Organic Chemical Vapor Deposition (MOCVD).

A demonstration of a critical current density of $640,000 \text{ A/cm}^2$ for a YBCO film fabricated by MSI on a buffered RABiT substrate supplied by ORNL was a key highlight of the project. Another highlight was the construction of a MOCVD reactor capable of producing lengths of superconducting tape up to 50m in length. Another highlight was the fabrication of up to 30m long biaxially textured Ni strips by WEC.

Should this project be continued further to scaleup, it would appear possible to fabricate long lengths of high- J_c YBCO wire by this process.

STATEMENT OF OBJECTIVES

The objective of this CRADA was to demonstrate a commercially viable process to make long lengths of YBCO tapes for superconductivity applications. The YBCO deposition method chosen by MSI was MOCVD.

MSI had the primary responsibility on establishing the technology base for continuous deposition of YBCO on RABiTS using Metal Organic Chemical Vapor Deposition (MOCVD). Particular attention was to be paid to the definition of handling, qualification and purification of the metal tetra-methyl-heptane-dionate complexes typically used as precursors for YBCO deposition by MOCVD. In addition to establishing process variables for high quality film deposition, various powder feed mechanisms, substrate heating methods and overall reactor design were to be considered.

WEC had the primary responsibility of establishing the process variables for producing long lengths of nickel tape which were suitable not only for annealing to produce a high degree of texture but also for directly feeding into the buffer layer and superconductor deposition processes without further surface preparation. Through a series of rolling and annealing trials, WEC was successful in identifying the appropriate degree of reduction per pass, total reduction, back tension and lubrication to achieve these goals while eliminating surface defects from the finished tape. WEC also provided guidance on the impact of coated conductor on the commercialization of Superconducting Magnetic Energy Storage systems in the form of a report.

ORNL was responsible for transfer of technology dealing with fabrication of all aspects of the RABiTS substrate and provide technical guidance by means of joint development for deposition of YBCO by MOCVD. ORNL was also tasked with providing buffered RABiT substrates to MSI for YBCO deposition. ORNL was also tasked to perform detailed microstructural, structural and superconducting property measurements of the materials fabricated by MSI and WEC.

BENEFITS TO DOE FUNDING OFFICE'S MISSION

The sponsoring office at the U.S. department of Energy (DOE) is the Office of Energy Efficiency and Renewable Energy. The project assisted the DOE Superconductivity Program for Electric Power Systems in meeting the program mission, which is to develop, with U. S. industry, the technological base needed to proceed to commercialization of electric power applications of high temperature superconductors. Long lengths of high performance are an integral component of any bulk, high temperature superconducting device. Hence, the project addressed the key superconducting element needed for superconducting applications to become a reality.

TECHNICAL DISCUSSION OF WORK PERFORMED

Evaluation of the MOCVD Process

MSI began the CRADA effort using a MOCVD reactor based upon a design developed by Professor Judy Wu at the University of Kansas (KU) under contract to MSI. The precursors typically used for MOCVD of YBCO are metal-ligand complexes with tetra-methyl-heptane-dione (thd) as the ligand. While the copper thd was known to be thermally stable, the barium and, to a much lesser degree, yttrium precursors were suspect in terms of thermal stability and resistance to moisture. The sensitivity to extended exposure to elevated temperature precluded the use of standard bubblers for delivery of the individual precursors in the vapor phase. Therefore, special handling and processing steps needed to be developed to ensure consistent YBCO film quality.

To that end, the reactor designed at KU utilized an earlier development at Hewlett-Packard in which the three metal-organic precursors are pre-mixed in a quartz tube and fed through a temperature gradient. In this way, the precursors are kept well below their sublimation and decomposition temperatures until immediately prior to vaporization. Although it was recognized that such a system was not appropriate for continuous deposition on long lengths of tape, it was decided to demonstrate the feasibility of using MOCVD in conjunction with RABiTS using this approach while exploring other precursor feed options for continuous deposition.

Early in the CRADA it was realized that the commercial precursor supply, particularly the barium thd, was erratic in quality. A subcontract was arranged with Professor Will Rees of Georgia Tech to provide MSI with expertise on precursor synthesis, purification, analysis, qualification and storage. As a result of the cooperative effort, MSI established in-house capabilities for the long term storage and handling of the environmentally sensitive thd precursors. Product quality as determined Thermogravimetric Analysis (TGA) was added

as a routine qualification procedure and as specification for the thd precursors was developed. A rigorous qualification procedure was established with two vendors of barium precursor to ensure a long term supply of quality product. The specification also resulted in sufficient process optimization at one of the vendors to result in a significant cost reduction in the precursor product. Any increase in volume purchasing should bring the cost of all precursors in the range of \$1/g. Although this may appear excessive, the quantities required per meter of tape are very small. Finally, Schlenk lines were built at MSI to allow for routine in-house purification of the yttrium and copper precursors prior to use in the reactor. All of these efforts had a significant effect on film quality and reproducibility.

Film development using the powder feed method progressed with the demonstration of YBCO films with critical current densities in excess of $1.5\text{MA}/\text{cm}^2$ on lanthanum aluminate substrates. The parameters and process steps used to achieve those results was then applied to short segments of RABiTS. The best result with RABiTS was a critical current density of $640,000\text{ A}/\text{cm}^2$ on a substrate where the ceria and yttrium stabilized zirconia (YSZ) layers had both been applied by pulsed laser deposition (PLD). This particular RABiT substrate had a configuration of Ni ($125\text{ }\mu\text{m}$) / CeO_2 ($0.9\text{ }\mu\text{m}$) / YSZ ($0.2\text{ }\mu\text{m}$). The YBCO film was $0.5\text{ }\mu\text{m}$ thick. Fig. 1 shows X-ray diffraction phi scans of the various layers, indicating good transfer of epitaxy from the Ni to the YBCO film. Fig. 2 shows a (112) pole figure for the YBCO film. Only ~80% of the YBCO film is c-axis-perpendicular and cube-textured (aligned with Ni). Almost ~20% was a-axis-perpendicular and rotated $\pm 11^\circ$ in-plane, as indicated in the pole figure. A small component consists of large crystals with apparently random orientations. Fig.3 shows J_c versus applied magnetic field for this YBCO film. The data is compared with a typical YBCO film on RABiTS grown using PLD. The field dependence for the MOCVD film appears quite similar the PLD grown YBCO film, perhaps with a slightly greater component of weak-links. Fig. 4 shows the temperature dependence of J_c for this YBCO film grown by MOCVD and a typical YBCO film grown using PLD on RABiTS. The difference in slopes is attributed to different types of defects structures in the films grown using the two different techniques resulting in different pinning structures.

Since this result was achieved, other films have been grown on buffered substrates where the buffer layers were deposited by various combinations of electron beam and sputter deposition. While films with excellent transition temperature and epitaxy with the YSZ layer have been grown, the early result with PLD buffer layers remains the highest recorded to date. Once the feasibility of using MOCVD to deposit YBCO on buffered RABiTS had been established, the effort at MSI shifted to consider the problem of deposition on continuous lengths of buffered tape. Various forms of precursor feed systems were examined in order to allow for continuous deposition. The first method tried relied on the addition of a load-lock chamber to the bottom of the reactor to allow for exchange of precursor feed tubes without breaking vacuum on the process chamber.

A pull-through tape feed system was designed and built to replace the substrate holder on the reactor. The system was capable of handling tapes up to one meter in length. The system was tested out in static runs on lanthanum aluminate substrates to establish the appropriate processing window for the new configuration. Since no buffered RABiTS was available in one meter lengths, it was decided to test the system using tape which was buffered with either ceria or yttria deposited by MOCVD. There was no expectation that high quality, aligned superconductor would be deposited on the tape during subsequent deposition trials but would allow for testing of the system configuration. As described above, the resulting deposition trials showed a banded structure indicating that either the powder feed method resulted in a pulsed flow of vapor to the substrate or the pull through mechanism was not smooth enough. The width of the bands was more consistent with the former possibility.

At that point, it was decided to proceed on the basis that continuous deposition, while based on the results achieved with static depositions, really required a complete change in reactor design to be properly tested. A commercial liquid feed system that relied on the precision metering of a solution of precursor through a vaporizer attached to the reactor by a feed tube was procured. In addition, a production prototype reactor was consigned that would be capable of processing lengths of buffered tape in excess of 50 meters in length. A substrate heating system more appropriate for uniform heating of a tape over large distances was also designed and ordered. The fact that MOCVD is not a line-of-sight deposition method was used to combine the best aspects of radiant heating and the ability to pipe warm process gases around obstacles to establish a uniform hot zone with smooth delivery of precursor to the substrate.

The liquid based delivery system was set up and tested on the development reactor while the production prototype reactor and substrate heating assembly were being fabricated. An appropriate solvent was identified for carrying the precursors which did not degrade subsequent film performance. A load-lock system for rapid introduction and retrieval of substrates without breaking vacuum was also incorporated into the reactor. Using a single solution containing the appropriate ratio of all three precursors, the liquid delivery system was optimized for film quality. Near the end of the CRADA, it was possible to make extended series of runs with resulting films of high quality and consistency. As an example, a series of six runs at identical conditions using lanthanum aluminate substrates yielded critical current densities in excess of $1\text{MA}/\text{cm}^2$.

Finally, the production prototype reactor was commissioned at MSI in early 1998. The reel-to-reel system, vacuum system and substrate heating assembly were all installed and tested. The liquid delivery system was not installed in the production prototype reactor by the end of the program due to the lack of availability of long lengths of buffered substrate. It was felt that optimization trials in the development reactor at static conditions were more important than merely demonstrating the continuous deposition on inferior substrates at that point.

Commercial Process for Textured Metal Tape

WEC performed an extensive set of rolling/annealing experiments in order to determine the appropriate conditions for rolling and annealing long lengths of nickel tape with the appropriate texture and surface finish for subsequent use as a substrate for epitaxial buffer layer and YBCO deposition. The thermomechanical schedules transferred from ORNL were successfully used to tapes up to 30 meters in length with thicknesses down to $37.5\mu\text{m}$ thick which showed, on subsequent heat treatment, textures as strong as $8\text{-}10^\circ$ FWHM in a phi scan. Subsequent depositions of buffer layers on WEC rolled material were successful in generating epitaxial growth of the buffer layers.

Impact of HTS Coated Conductor on SMES Applications

WEC conducted a preliminary investigation to determine the impact of HTS wire based on coated conductor on SMES applications. The main conclusions were that the intrinsic stability of the coated conductor will probably not require micron size filamentary

structures, that thick films (up to 100 μ m in thickness) are necessary for usable conductors, that current densities in the conductor should be greater than 100kA/cm² to be of interest and that new techniques in both conductor fabrication and field shaping are necessary for the rapid ramping needed for power quality SMES magnets. In addition, these superconductors must be available at less than \$70/kA m to be considered at all and can result in 30% reductions in net present value cost if they are available at present day low temperature superconductor (LTS) cost of less than \$10/kA m. Finally, the benefit of HTS coated conductor diminishes rapidly as the stored energy increases and refrigeration becomes a smaller element of the total system cost.

Summary and Conclusions

- 1) MOCVD is a viable candidate for manufacturing long lengths of high quality coated conductor.
- 2) Rigorous control of precursor quality is required for consistent film properties.
- 3) Long term, continuous tape processing may require splitting the feed system into two liquid feed sources (one for barium and one for a mixed solution of yttrium and copper) to allow for tuning the vaporizer temperature more closely to the vaporization temperatures of the individual precursors and provide the opportunity for longer operation times between system shutdown.
- 4) Precursors which are liquids at room temperature would maximize the delivery rate of a liquid feed system by eliminating the need for dilute solutions of precursor powder in solvents.
- 5) Rolling and annealing of nickel tape to long lengths and thin sections while maintaining high texture and good surface finish appears to be a very robust process.
- 6) HTS coated conductor could have a cost advantage in smaller SMES systems where the superconductor cost dominates the system if cost levels similar to those for present day LTS wire are achieved.

INVENTIONS

None to report

COMMERCIALIZATION POSSIBILITIES

MSI is currently seeking to raise finances to carry the project further. If successful, the company will take this process to the next scale-up step.

PLAN FOR FUTURE COLLABORATION

Should MSI obtain the necessary finances to continue the project, ORNL expects to actively collaborate with MSI in scaling up the process.

CONCLUSIONS

This CRADA was successful in demonstrating the use of MOCVD as a viable method for fabricating high- J_c YBCO films on RABiT substrates. Transfer of technology from ORNL to WEC resulted in the fabrication of up to 30m of textured Ni tapes.

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