MOCVD of Coated Conductors in Braunschweig

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***Abstract* - A MOCVD approach to process superconducting Coated Conductors is described and recent results obtained at PerCoTech and IOT (TU-Braunschweig) are presented. Advantages of an all-chemical approach in general and MOCVD in particular are explained. The feasibility of Coated Conductor production, inclusive buffer layer, in a one-path MOCVD system, and the technical and economical aspects of scaling up are discussed.**

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I. INTRODUCTION

Buffer and superconducting layers for Coated Conductors (CC) on metallic substrates can be produced by physical methods like Electron Beam Evaporation, Laser Ablation or alternatively by chemical solution or vapour deposition techniques. In many countries superconducting layers are fabricated by Metal-Organic Chemical Vapour Deposition (MOCVD). In USA this process is used by SuperPower, MetOx and ORNL, in Japan by Chubu, in South Korea by KAERI and China (in Changchun, Jiangsu and Xiamen) and in Europe by LMGP (Grenoble, France), SuperOx (Moscow, Russia) and PerCoTech / IOT (Braunschweig, Germany).

Several European companies develop cables, motors, fault current limiters, magnets and other machines utilizing CC, which are the 2nd generation (2G) of high-T_c (HTS) wires. Unfortunately, no European conductor manufacturer is able, at present, to deliver 2G wires in quantity sufficient to cover the demand. To make Europe competitive, one should choose the most promising fabrication approach to establish a 2G production line. As most promising we see methods, which make it possible to fabricate large amounts (continuous lengths) of high-quality CCs at lowest possible cost.

It is noteworthy that at this juncture SuperPower, which uses MOCVD to fabricate the superconductor and PVD (Physical Vapour Deposition) for the buffer layers, obtained the longest and highest quality CCs. Both MetOx and PerCoTech demonstrated the feasibility of MOCVD buffer layers on textured metal tapes. Indeed, we believe that all-MOCVD and MOCVD of superconductor on CSD (Chemical Solution Deposited) buffer are the two most promising low-cost techniques for 2G wires. In this paper we report only on the MOCVD development activities in Braunschweig, Germany. It is a collaborative effort of PerCoTech AG and IOT (TU Braunschweig).

II. EXPERIMENTAL

The metallic substrate material used was textured alloyed Ni5at%W tape, 10-mm-wide, produced by EVICO, Dresden, and Forschungszentrum (Research Center) Karlsruhe (FZK). Such textured substrate was chosen, because only PVD techniques can produce textured buffers on non-textured metal (stainless steel, for example) tapes. We decided to avoid any PVD techniques, because of economic considerations.

The superconducting oxide compound to be deposited is $YBa_2Cu_3O_{7-\delta}$ (YBCO). All precursors have thd ligands (thd = tetramethylheptanedionate), are solved together in a solvent (diglyme or xylene), and are evaporated in a single source evaporator. Our precursor delivery system is the so-called band evaporator, developed at IOT and PerCoTech, and published in detail elsewhere [1]. The liquid solution of the precursor compounds of Y, Ba and Cu is fed into this evaporator, but only the precursor material is transported to the deposition chamber. The solvent is separated and recycled after condensation in a cooling trap. In contrast to other common solution-based evaporator techniques, such as injectors, no solvent vapour is burnt in our deposition process. This enables us to obtain high deposition rates in our MOCVD reactor, and at relatively low deposition temperatures and oxygen gas flow. It is easier to control the oxygen partial pressure and prevent the deleterious $BaCO_3$ formation, because the high CO_2 partial pressure is supressed.

Usually, the surface temperature depends on the emission coefficient of the tape, which during the layer growths changes from mirror-like to black. Our MOCVD reactor is an almost fully thermally isolated hot wall system, enabling us to stabilize the surface temperature of the coated tape during the growth. Additionally, the electrical heating power consumption is minimized.

The reel-to-reel (RTR) design is constructed without reverse roller, as it would be necessary in a helix tape system[I]. In our first scaling-up step, the tape speed is determined only by the length of the deposition zone at the chosen growth rate. The next planned scaling-up step will involve both width and length of the zone, *i.e.*, wider tapes will be used, which can be cut after deposition into the needed width. Recently only one side of the tape is coated (as it is considered for the next scale up step), although generally a hot wall reactor can be used for double side coating.

We are convinced that a minimum of tape handling and no deformation at high temperature are both critical for avoiding defects. Therefore, mechanically moved reactor parts should be avoided at high temperature and in the vacuum. The only mechanically moved parts are the two reels and the two rollers in the band evaporator, all located in cold zones. In the new MOCVD RTR-system the buffers and superconductor will be coated in a single path.

The present tape velocity for the buffer layer is 10 m/h. This speed is planned for the YBCO layer too. In our old MOCVD-RTR-system, YBCO has been coated with a tape velocity of 3-6 m/h. Within the last two years, the YBCO and buffer layers fabrication processes at PerCoTech were scaled up from hundreds of mm to over 10 m lengths. Therewith the buffer layer deposition rate was increased three times. The next planned scale-up step of the all-MOCVD CC fabrication will aim towards a 10-20 m/h process, with the buffer layers and YBCO being deposited in one path.

[I] In the helix system the tape passes several times through the deposition zone in parallel direction. For each pass a minimum of two reverse rollers are needed, in order to return the tape into the deposition zone.

At present, we plan to protect the superconductor by a thin Ag-layer. This layer might be deposited by PVD-technique, because it is a process available to us. Additional other stabilization layers or tapes can be added.

III. RESULTS

The results described below were obtained for MOCVD layers deposited at 3 to 6 m/h tape speeds. Figure 1 shows the all-MOCVD CC made at PerCoTech and wound on a cylindrical former. Inductive and direct-current (dc) measurements were performed on different (MOCVD / CSD) all-chemically obtained CC after they have been coated with silver (by electron beam evaporation at Zenergy Power or THEVA).

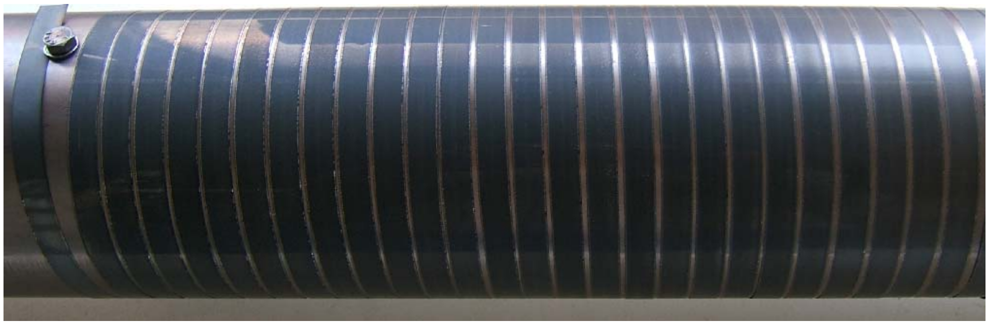

Fig. 1. All MOCVD-Coated Conductor (10 m long).

Figure 2 shows typical inductively measured I_c data along a 10 m section of our CC. The comparison with similarly measured I_c profiles for YBCO(MOCVD)/CSD-buffer tapes shows, in spite of a comparable maximum j_c, an accentuated j_c fluctuation in our all-MOCVD CC. Such high deviations of j_c might be caused by the initial condition of the Ni tape surface. It was coated as delivered without any cleaning process or initial quality control.

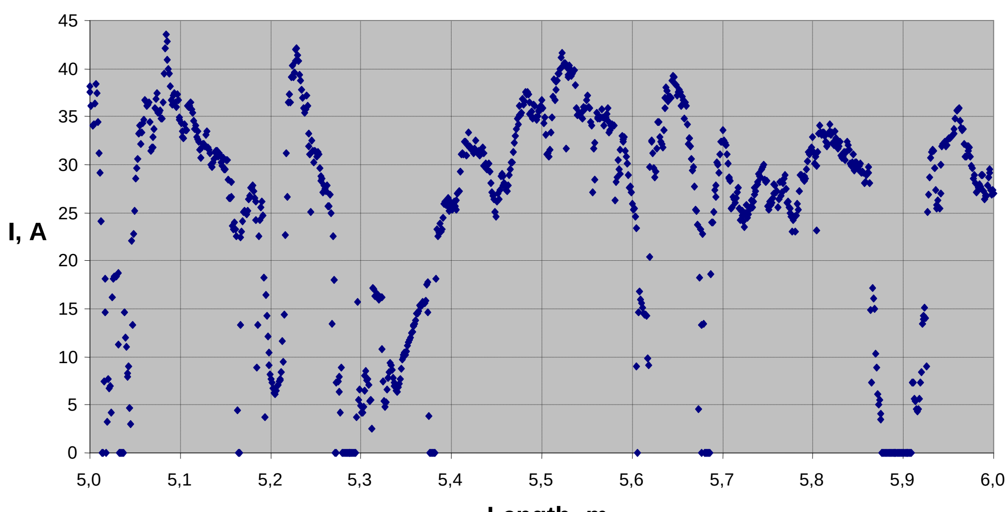

Fig. 2. Inductively measured I_c of a 1 m segment of a 10 m long all-MOCVD CC. The I_c over ‘good’ 0,1-0,2 m CC segments is 25-40 A. The YBCO thickness was ~350 nm, which corresponds to maximum current density j_c > 1 MA/cm^2. The Tape Star (THEVA) measurement was performed at Zenergy Power [2].

The producer acknowledged many defects after the delivery of this tape. These defects were caused by the cleaning procedure after rolling and crystallisation, but should be now significantly reduced by an improved cleaning process. Additionally, it is known that epitaxial growth of several oxides on textured metals can be determined by the chemisorbed sulphur monolayer. At least two sulphur superstructures *p*(2×2) and *c*(2×2) on Ni (001) surface are known. An incomplete *c*(2x2) S superstructure leads to different in-plane oriented oxide growth, which results in reduction of j_c. So the surface state of Ni tape should be well defined and constant over the lengths in use. Efforts to attain a stable, homogeneous and reproducible surface quality of Ni-tapes over long lengths are being pursued in collaboration with EVICO.

To further evaluate the quality and potential of our MOCVD process, we deposited YBCO on substrates with buffer layers differently prepared by different laboratories. Below, we show two examples of data obtained on such samples.

Figure 3 shows the dc *I-V* curve of the worldwide simplest structure: MOCVD-YBCO/CSD-LZO[II]/NiW-tape (CSD buffered tape prepared by Nexans SC). The architecture of the 4.4 m long sample is shown by the upper left inset. The end to end direct measured I_c over a short length of only 110 mm was 57.9±0.28 A (n-value = 22.4±1.1), however over the 4.4 m the I_c = 21.0±0.2 A (n-value = 9.8±0.5).

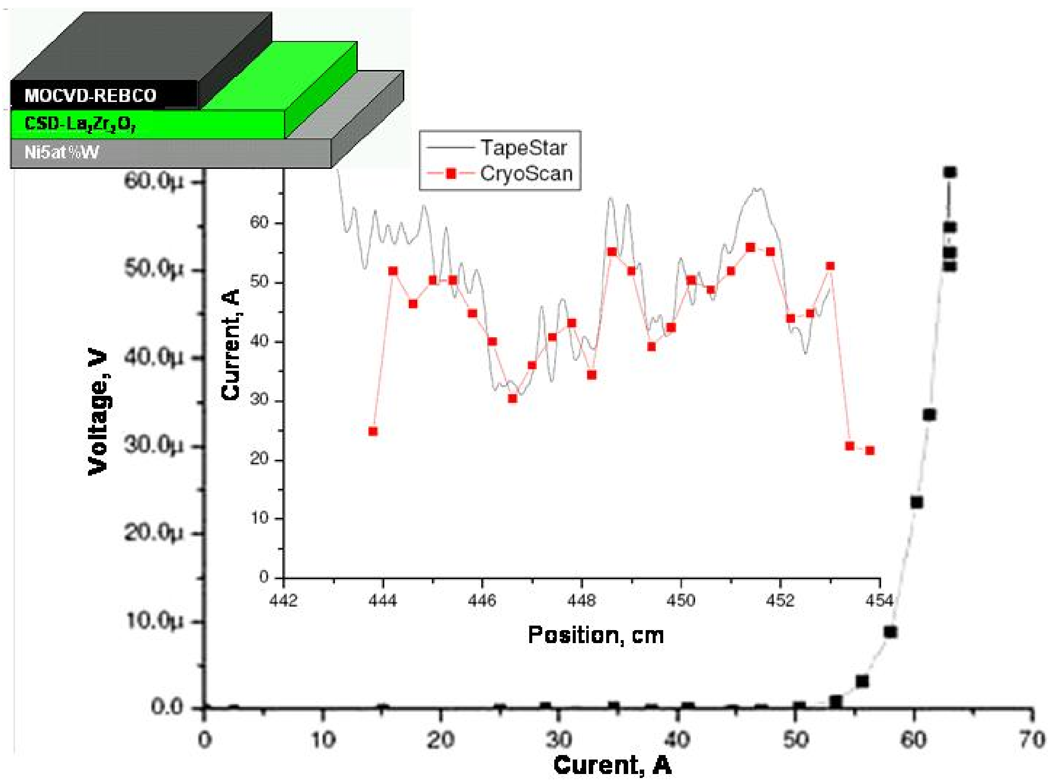

Fig. 3. Direct current measurements of MOCVD-YBCO/CSD-LZO/NiW. End-to-end critical current was measured as 57.9±0.28 A/cm-width (0.1 m piece of a 4.4 m long tape, which had an end-to-end critical current of 21.0±0.2 A). The inductively measured I_c value is shown in the inset. The CSD-buffer was produced by Nexans Superconductors and the critical currents were measured at THEVA by "TapeStar" and "CryoScan" [3] apparatus.

The upper right inset shows the I_c variation inductively measured by two different apparatus. The local strong depression of I_c must be caused by inhomogeneities and defects. The origin

[II] LZO – $La_2Zr_2O_7$

of those could be multiple: Ni-tape surface defects or dust, LZO or YBCO process deviations. So far no clear evidence for YBCO-MOCVD process instabilities was detected by Scanning Electron Microscopy, Energy Dispersive Analysis and X-Rays Diffraction of the samples.

The j_c of 0.2 m-long samples taken from the opposite ends of the tape of Figure 3 was measured by "CryoScan" at PerCoTech. Table I shows that average j_c values were nearly the same for both samples.

Table 1. The j_c data of 0,2 m long sections taken from the opposite ends of the tape of Figure 3.

Thickness, *nm*	max j_c, *MA/cm²*	min j_c, *MA/cm²*	ave$_{(95\%)}$ j_c, *MA/cm²*	I_c, A		
				max I_c	min I_c	ave$_{(95\%)}$ I_c
700	0.93	0.35	0.65±0,15	65	25	46±11
700	0.89	0.37	0.65±0,12	62	26	46±8

Second example is I_c data of MOCVD YBCO deposited on a composite CeO_2/LZO buffer deposited by CSD on NiW, which was fabricated by Zenergy Power. Figure 4 shows the I_c profile determined over the whole length of a 2.5-m-long buffered tape section, which was measured by "TapeStar" at Zenergy Power. The average I_c of about 35 A corresponds to an average $j_c \approx 1.4$ MA/cm^2, but at few points the local I_c is very low. Again, defects of yet undetermined origin must be at play.

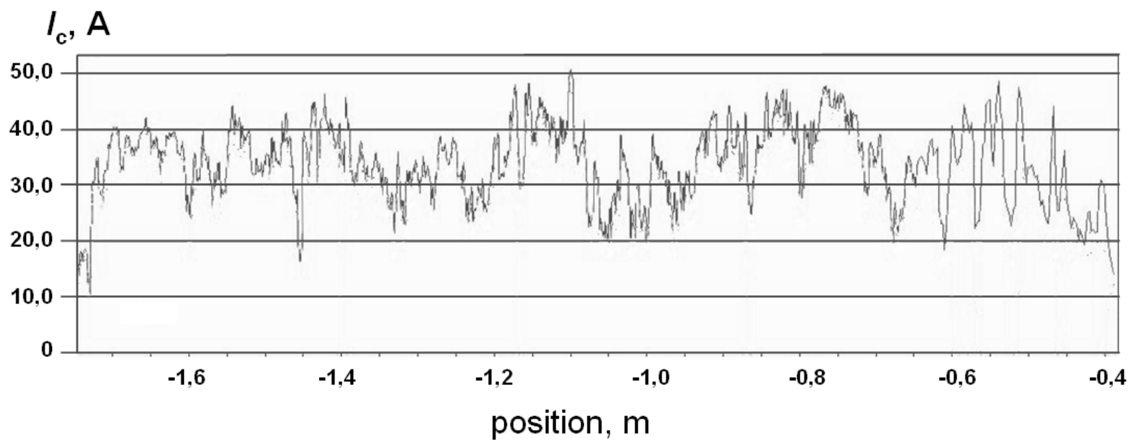

Fig. 4: Data of I_c measurement of 2.5 m of MOCVD-YBCO/CSD-CeO_2/CSD-LZO/NiW. CSD buffers were produced and measurements performed by Zenergy Power.

Over the past months, the development of thicker YBCO for higher currents has been performed. The main work consists of optimization of multilayered growth of YBCO via tuning the process conditions and YBCO composition. The current status of this work is characterised by local and average j_c values for tape lengths of about 1 m given in Table II.

Table II. The j_c data of nearly 1-m-long tape coated with MOCVD-YBCO.

thickness *nm*	max j_c, *MA/cm²*	min j_c, *MA/cm²*	ave$_{(95\%)}$ j_c, *MA/cm²*	I_c, A		
				max I_c	min I_c	ave$_{(95\%)}$ I_c
900	0,96	0,58	0,76±0,16	86	52	68±14
1200	0,81	0,30	0,54±0,14	97	36	65±17

Our current goal is to obtain by the beginning of next year (2010) a maximum I_c value of 150 A/cm on all-chemically fabricated CC of 1 m length. We expect a carrying current of at least

100 A over at least 10 m long CC. Although the worldwide simplest all-chemical-approach (MOCVD-YBCO/CSD-LZO/Ni-tape) could set some limitations (*e.g.*, by the single buffer layer is a weaker diffusion barrier) to the final superconducting performance, we use it for thick MOCVD-YBCO. An optimized YBCO process might be used on twice-buffered tapes (either all-MOCVD or in combination with CSD), if it is allowing higher currents. Thereby, the elimination of Ni-tape defects and inhomogeneities coming from buffer process is already in focus. We develop the all-MOCVD and MOCVD-HTS with CSD-buffer (CSD by NSC or Zenergy) approaches in parallel.

IV. ECONOMIC ASPECTS OF MOCVD

Chemical deposition methods are expected to enable low cost CC production. In the US, American Superconductors and SuperPower already established CSD and MOCVD for the superconducting layer of coated conductors of relatively long lengths [4,5]. In Europe, several groups develop chemical deposition techniques for the buffer layer system, but only 10-50 meter long tapes could be demonstrated until now. However the all-chemical deposition approach will eventually offer many important economic advantages:

a) A single CSD-LZO buffer layer on textured Ni5at%W enables the deposition of MOCVD-YBCO layers with critical current densities up to 2 MA/cm^2 at 77 K. Complicated buffer layer systems, which might cause lower production yield and increase the investment and personal costs, could be avoided. Other buffer layer systems produced by PVD techniques usually need 3 buffers (AMSC) or 5 buffers (SuperPower).
b) All-MOCVD can be applied in a single RTR deposition system. Generally, the yield of production units is strongly influenced by the mechanical handling of the tapes. Many faults could be avoided by using a single RTR deposition system. The yield of the production can be thus improved and the costs reduced.
c) All-MOCVD can be operated with lesser number of personnel. Usually, specially trained workers are needed for physical, ion beam or chemical deposition methods. The general design of the MOCVD-deposition units is the same. Therefore, all deposition units can be operated by the same persons.
d) All-MOCVD can reduce the investment costs. All deposition units are fabricated on the same basis, because they have the same design. All deposition units can be easily combined in a single RTR deposition system and a simple pumping system can produce low vacuum without complicated connections between the deposition units.
e) MOCVD systems are compact and can be scaled up at a relatively low cost (Figure 5). The deposition zone is rather short, because the local YBCO deposition rate is 20-40 µm/h. In fact, rates higher than 40 µm/h were also reported [6]. A deposition zone of only 40 mm x 1000 mm enables a throughput of 200-400 m/h of 4 mm wide tape. The precursor gas distribution is controlled by the showerhead, which has to be adapted to the size of the deposition zone. The evaporators can be scaled up by the increase of gas flow rates and the capacity of precursor solution delivery system. Low vacuum allows simple maintenance of the vacuum chamber.

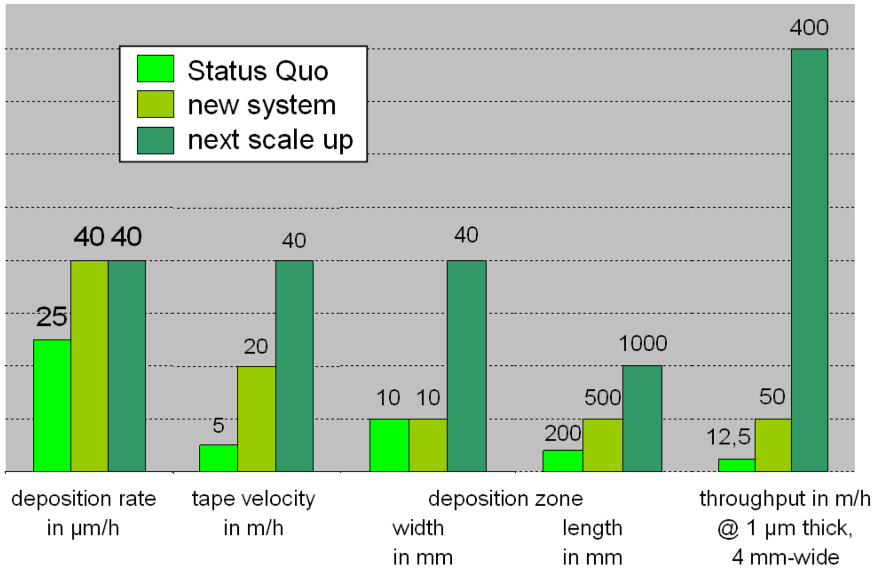

Fig. 5. Scale up plans for MOCVD of YBCO (Braunschweig activities only).

Although we did not yet establish commercial production of CCs, the recent precursor costs are approximately few €/m–10mm width (1 µm thick superconductor). The price would be significantly reduced when precursors would be needed for a production of 1,000 km/year. Based on the estimate that the precursor price halves when its volume increases10 times, the precursor costs would be only approximately 0.5 €/m. We calculated that in the case of all-MOCVD the costs for buffers and superconductor are dominated by the cost of the metal tape.

V. CONCLUSION AND OUTLOOK

The chemical techniques (MOCVD and CSD) should enable us to produce low-cost CC wires. The scaling up of MOCVD process is simpler than of PVD techniques. It needs only the furnace and the gas distribution unit to be enlarged while no expensive vacuum is necessary. The MOCVD deposition chambers for buffers and superconductors have the same design and MOCVD can produce Coated Conductors in a single path starting from the textured Ni tapes with speeds on the order of tens m/h. At present, 10-m-long sections of MOCVD Coated Conductors were demonstrated. The maximum inductively measured I_c of YBCO on chemically coated buffers was exceeding 90 A/cm-width and the goal is to obtain by the beginning of next year a maximum I_c value of 150 A/cm-width. Currently, we develop the MOCVD-YBCO on CSD and MOCVD buffers in parallel. The elimination of substrate tape surface defects is addressed, and the characterization of long tape sections by resistive I_c measurement represents the task to address once these defects are eliminated.

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