

Reactive Co-Evaporation of YBCO for Coated Conductors

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Abstract-- We describe methods for depositing high temperature superconducting films on textured metal tapes by reactive co-evaporation (RCE). We discuss how RCE can be used to deposit on moving tape in a continuous fashion in a Garching-style process. Results are presented on films deposited by RCE at Los Alamos on IBAD-MgO textured tapes. The performance achieved, attaining over 500 A/cm-width in self-field at 75.5 K, is competitive with the best results obtained by other processes for coated conductors. Tape production throughput is critical for the economics of the process and high deposition rates achieved in RCE are attractive for this. We present a detailed cost analysis model for HTS deposition using an RCE Garching process. The results indicate that HTS deposition can cost < \$5/kA·m in a scaled up manufacturing environment.

1. INTRODUCTION

A number of film deposition methods for high temperature superconductors (HTS) have been demonstrated to be successful in fabricating coated conductors [1]. They include physical vapour deposition (PVD) methods such as pulsed laser deposition and co-evaporation, as well as metal-organic chemical vapor deposition (MOCVD) and solution methods. Some of them are two-step processes, where an amorphous film is deposited first and the HTS structure crystallizes subsequently. Others are one-step processes, also known as *in-situ* processes, where deposition and crystal growth are simultaneous [2]. The speed of HTS film growth is a critical factor for achieving economically viable manufacturing processes. Manufacturing economics dictates that methods which produce high quality films *and* which are scalable to large areas and high rates of film growth be preferred. Some HTS deposition processes are not easily scalable. The HTS growth rate is also limited in various deposition processes, sometimes for multiple reasons. This is important for the final economics of the process.

Here we describe one type of reactive co-evaporation (RCE) method where one alternates between deposition and oxidation on a fast time scale. In spite of the sequencing of the two steps, we call this a one-step or *in situ* growth process, due to the fact that the deposition steps are done at a sub-unit cell thickness. By doing this oscillation of processes one can achieve high instantaneous deposition rates while the average film growth is at a lower rate. Although the principle for this

process was developed over 15 years ago for a different reason, mainly to keep the background pressure low during evaporation, the process has inherent advantages in scaling to high film growth rates, necessary for coated conductors [3].

Currently MOCVD and solution deposition (commonly referred to as MOD) are two preferred methods for coated conductors by US industry [4]. The companies have achieved lengths of 100s of meters in a prototype manufacturing environments [4]. Several groups, most notably Theva GmbH in Germany [5] and KAIST/KERI in South Korea [6] use the oscillatory RCE method for making coated conductors in lengths of 10s of meters. Our approach is similar to these, in principle, but the tape transport method we propose is novel and we believe more amenable to manufacturing.

2. 'GARCHING' DEPOSITION PRINCIPLE

Kinder and coworkers first demonstrated a co-evaporation process for $\text{YBa}_2\text{Cu}_3\text{O}_y$ (YBCO) films with the alternating deposition and oxidations steps [3]. This was achieved with a heater in which the substrates rotate on a turntable between an oxygen pocket, where the oxygen pressure is sufficiently high for stability of HTS compounds, and a deposition zone where the oxygen pressure is lower to allow evaporation; see Fig. 1. In practice this pressure difference is achieved by making the opening for the oxygen pocket, where the samples pass through, with a very small cross sectional area. During the entire process the sample is kept within the heater that approaches a black body, esp. in the oxygen pocket. This type of heater with an oxygen pocket solved two key issues for HTS film deposition: (1) achieving a high oxygen pressure needed for HTS materials while the deposition chamber was at a lower pressure, and (2) a uniform and stable substrate temperature during film growth, which was also not easily achievable prior to this invention.

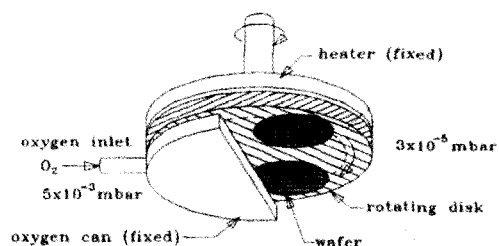


Fig. 1 Schematic of the original 'Garching' heater with a rotating substrate turntable.

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Samples oscillate between a deposition zone and an oxidation zone; following Ref. [3]

Fig. 2 shows the p-T temperature diagram with the stability line for $\text{YBa}_2\text{Cu}_3\text{O}_y$ (YBCO) from Lindemer et al [7] drawn in. Kinder's process essentially meant that the film was deposited in the low-pressure regime where it was not necessarily thermodynamically stable, but then cycled to a thermodynamically stable region for a short time before the deposition was done again. Although not a priori obvious that this process would work, it has been thoroughly demonstrated over the last 15 years at the laboratories at TU München (Garching) as well as at other laboratories and in commercial production at companies including Theva GmbH [8] and Conductus Inc [9].

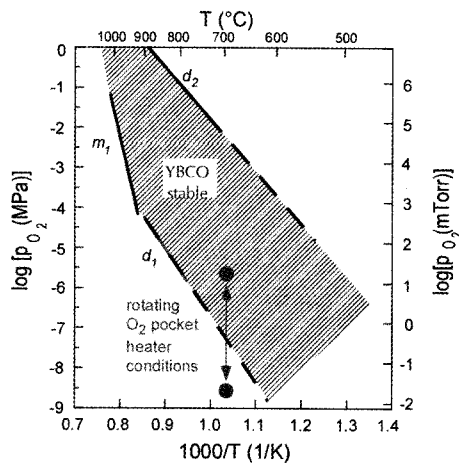


Fig. 2. $p_{\text{O}_2}(T)$ diagram in Arrhenius representation, showing the region of YBCO phase stability as well as the operating points for deposition and oxidation in our process.

In the past decade a number of groups have applied this process for fabricating coated conductors. We describe here three notable implementations. They differ in how the tape passes through the system and how oxygen is delivered.

A) Theva method

Early on in coated conductor development Theva developed a practical RCE approach using a new oxygen pocket innovation called an “oxygen shuttle.” [5] Oxygen is introduced using an oscillating oxygen box underneath the tape, as pictured in the schematic in Fig. 3 (a) Initially thermal co-evaporation was used to deposit the HTS films, later to be replaced with a single e-beam evaporation source. The advantage of their approach is that tape speed is independent of the oxygen pocket oscillation as the two can be adjusted separately. Reel to reel transport allows for continuous deposition on long lengths of tape. Note that the oxygen shuttle always blocks part of the vapor stream so the utilization is somewhat reduced in the optimum deposition zone.

(B) KAIST method

Another approach was taken by Youm and coworkers at KAIST in South Korea [6]. They used a rotating cylinder

that carries the sample. A bottom section of the cylinder is exposed to the vapor flux for film deposition and the rest of the cylinder is at a higher oxygen pressure; see Fig. 3 (b) The method is also called cylindrical sample holder in a dual chamber (CDC), with one chamber being at low pressure and the second at high oxygen pressure [6]. This is an analogue of the original Garching turntable heater and similarly, it is very robust in addressing homogeneous sample temperature since the samples are in a ‘black body’ for much of the time. Deposition zone is placed at the optimum vapor position with 100% utilization within the window. The KAIST implementation results in a limited length for the coated conductor since the tape was wrapped around the cylinder in a spiral and thus the deposition was done in a fixed batch mode. Their original heater could accommodate an 8 meter long, 1 cm wide tape, and a subsequent scale up was made for 100 m long tape [6]. A scale up to longer lengths with this approach was not practical due to the chamber size requirements.

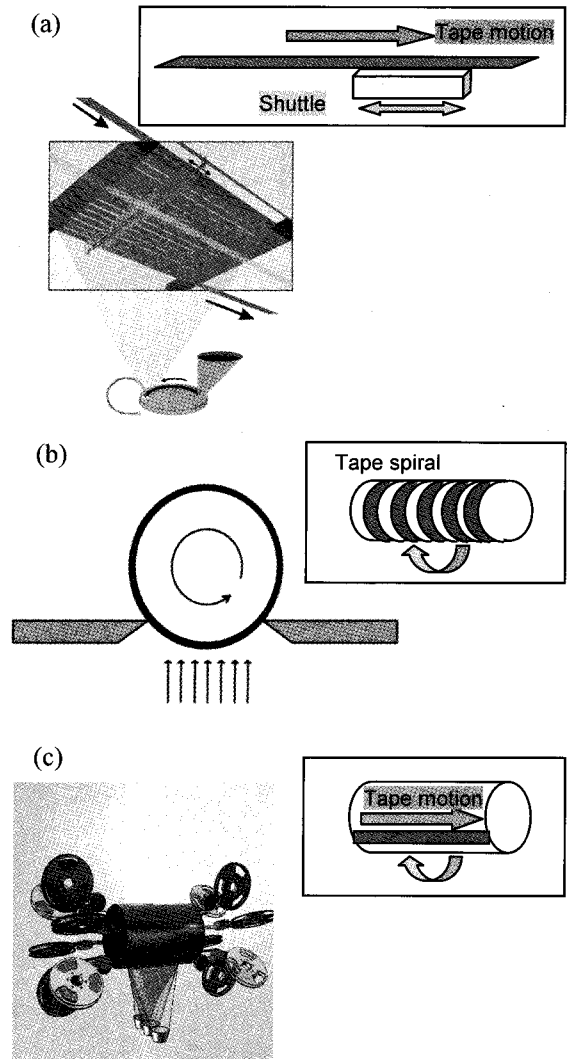


Fig. 3. Illustration of the various implementations of the Garching process for coated conductors; following Refs. [5,6,10]. a) Theva method, b) KAIST method, and c) LANL method.

(C) LANL method

Storer et al. [10] at Los Alamos discussed essentially a similar approach as KAIST, but with additional reel-to-reel tape transport. By allowing tape travel in the direction of the cylinder axis, this tape transport method leads to the separation of the oxygenation motion from the tape transport, as shown in Fig. 3 (c) This is analogous to the tape transport in the Theva method, but keeps the robust cylindrical black-body heater of the KAIST method. The addition of reel-to-reel motion makes the deposition significantly more compact compared to the KAIST heater, e.g. a 10 cm diameter heater can be used to deposit on multiple tapes which can be more than 100 meters long. If a multiplicity of reels with wider tapes were to be used, populating the circumference of the cylinder, a high vapor utilization efficiency would also be obtained.

3. EXPERIMENTAL DESCRIPTION

We use elemental sources of yttrium, copper, and barium. The former two are heated using a differentially-pumped Pierce-type electron gun which is skipped between them and the latter is conveniently heated using 400 kHz RF induction. Atomic absorption is used to measure the vapor densities just beneath the tapes. These data are used in real time to adjust the RF power, as well as the electron beam scan patterns and residence times.

As discussed in the previous section, our samples alternately move from a low-pressure region, where they receive a deposit from the sources, to a high-pressure region, where they are oxidized and YBCO is thermodynamically stable. The stability region is shown in Fig. 2 as the gray region, which has been determined by Lindemer *et al.* [7] A rotation speed of 5 Hz results in a coating time of 20 ms and an oxidation time of 180 ms. The ratio of coating time to oxidation time is therefore 1:9. With an instantaneous YBCO deposition rate of 6 nm/s, approximately 0.12 nm is deposited per pass. In this way a 1 μm thick film can be produced in 30 minutes. We have determined that the rotation speed can be reduced to 2 Hz (0.3 nm per pass) with essentially no change in YBCO properties.

In our experiment, tape sections are mounted parallel to the rotation axis of a heated drum. With the tapes mounted this way, transport along the tape direction would permit long lengths to be produced. In our lab-scale experiment, however, one to four tape pieces are mounted on a 10 cm diameter drum and they do not move lengthwise. The deposition temperature is between 750 and 800°C.

We investigated the influence of composition on the properties of the superconducting films and found that there was good agreement with previous co-evaporation results [11]. In general, films which are slightly Ba deficient had higher J_c 's. The copper content did not play as vital a role, as long as the composition was close to 123 stoichiometry. Fig. 4 shows the approximate region of composition for the best films within the Y_2O_3 -BaO-CuO ternary diagram.

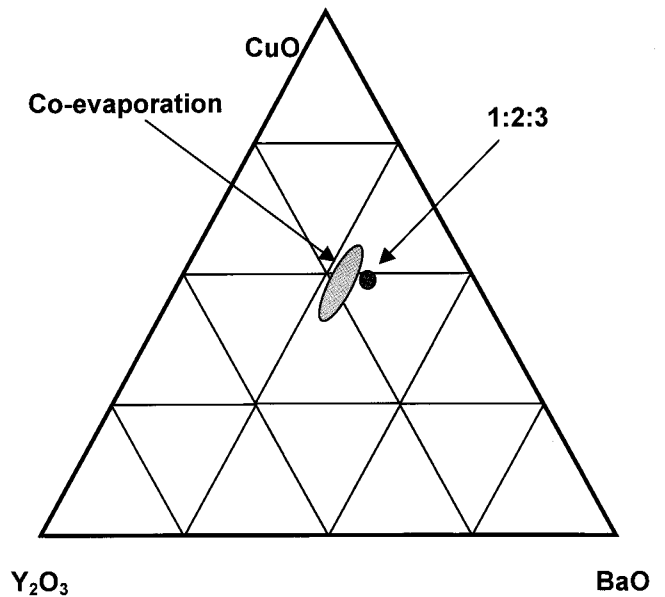


Fig. 4. Y_2O_3 -BaO-CuO ternary phase diagram. The oval next to the 123 stoichiometry represents the compositional range of the films with the highest critical currents.

We measure superconducting critical currents at 75.5 K and in an applied magnetic field of 0.6 T perpendicular to the tape. An applied field, provided by small permanent magnets, is used in order to limit the critical current. A lessened critical current removes the possibility of tape heating and tape damage, and provides us with a way to quickly determine the sample quality over a full cm width.

4. RESULTS

Critical currents have been measured as a function of YBCO film thickness. As shown in Fig. 5, I_c for our best samples rises monotonically with film thickness, but with a slightly decreasing J_c . The self-field critical current values are typically 5 times larger than the 0.6 T values, thus a 100 A in 0.6 T corresponds to 500 A without applied field. These samples have zero-field J_c values between 2.5 and 2.9 MA/cm^2 .

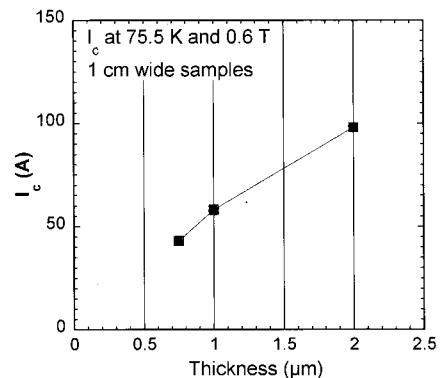


Fig. 5. Critical current in a field of 0.6 T vs. YBCO thickness for the best RCE samples.

The samples were grown slightly Ba-poor as described previously. TEM cross sections, shown in Fig. 6, show the typical columnar morphology of PVD YBCO films, as well as dislocations and Y-O, Y-Cu-O secondary phases. CuYO_2 and Y_2O_3 have been reported earlier in films grown under similar thermodynamic conditions[11]. Usually Y_2O_3 grows in two different forms. Either, 10-15 nm thick slabs as seen in Fig. 7 or in small (4-5 nm) size dots that are lined up along a line. This line is almost always at an angle to the YBCO-buffer layer interface. While the slab shaped Y_2O_3 particles are expected to help flux-pinning along a-axis, Y_2O_3 nano-dots should help flux pinning at an angle to the c-axis. Most of the CuYO_2 precipitates appear to grow along the c-axis and improve the c-axis flux pinning. Round CuYO_2 precipitates as seen in Fig. 6 may help random pinning to increase the overall in-field properties of the wire.

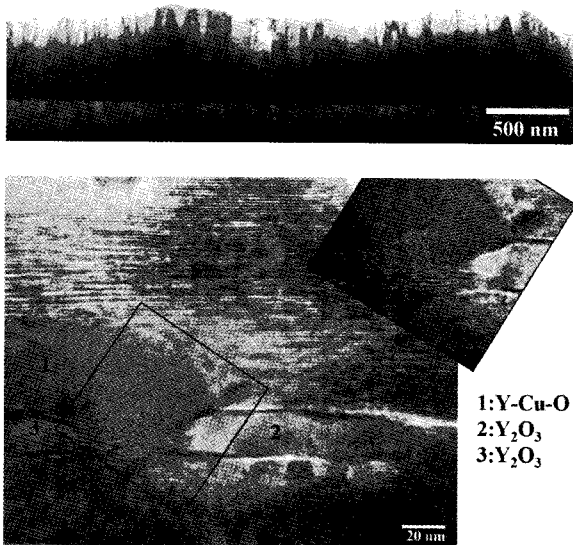


Fig. 6. TEM cross sections with low to high resolution showing columnar structure and secondary phases.

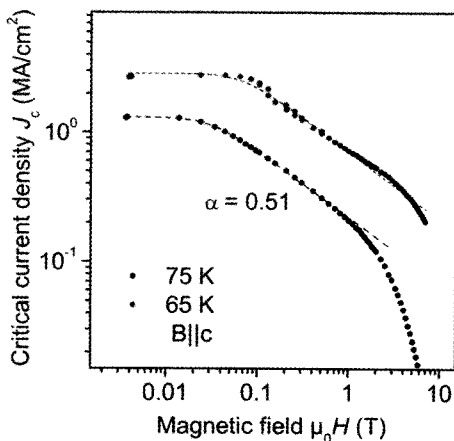


Fig. 7. Critical current density as a function of magnetic field for the sample with highest J_c .

The sample of highest J_c made to date in our system had an J_c of 590 A/cm in self field. It was a 4.5 μm thick film with a J_c of 1.3 MA/cm². The magnetic field exponent α ($J_c \propto B^{-\alpha}$) for the critical current was measured to be 0.51, see Fig. 7. An α value close to 0.5 is typical for YBCO thin films without additional nanoparticles and can be explained by shearing of flux lines in between strongly pinned ones as dominant depinning mechanism. The angular dependence of J_c on the magnetic field is shown in Fig. 8. Remarkable is the relatively low c-axis peak in this sample, which seems to be in contrast to the columnar defect structure and c-axis dislocations seen in TEM. We found that the c-axis peak decreases with film thickness and with temperature. Additionally, it depends strongly on the composition of the sample. The columnar growth defects might become ineffective as pinning centers at high temperatures and/or film thickness and additional, artificial pinning centers might be necessary to increase J_c further.

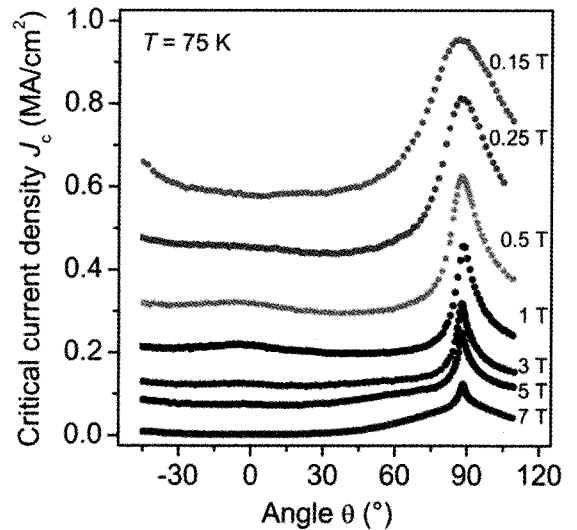


Fig. 8. Angular dependence of the critical current density for the sample with highest J_c .

5. RCE COST MODEL

Economics of a production process depend critically on the throughput and the performance achieved. We already discussed the performance of the YBCO layers that we demonstrated to date. For the purposes of this cost model, we will assume that a 2 μm thick film of HTS can carry 500 A/cm in self field. In order to compare this process to other competing processes, we developed a cost model for a scaled up production using RCE. Fig. 9 shows the cross-section of a cylindrical (drum) heater with a multiplicity of tapes used in the model. The actual tape number and tape widths do not enter the model, only the total tape width, but it is assumed that the tapes are slit at the end, thus the tapes could be 2–10 cm wide.

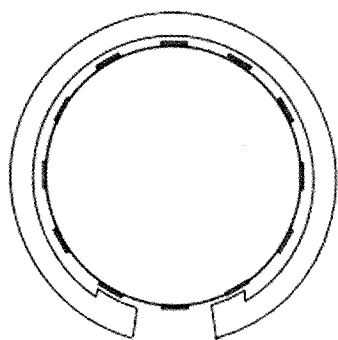


Fig. 9. Cross section of the cylindrical heater with tapes.

Table 1 shows the process parameters used in our model for a single deposition system. An important feature of this process is that the instantaneous deposition rate can be very high, in this case assumed to be 7.5 nm/s, even though the time-averaged film growth rate is 10 times lower, due to the fact that a number of tapes are being coated simultaneously on a duty cycle. We further assume a materials utilization rate for the evaporation process of 10%.

To estimate the capital expenses needed for this kind of deposition we put together what we believe are reasonable costs for the various critical components. These components are technologically available, but may need some significant additional engineering to implement, such as the heater with the tape transport creel, the chamber and evaporation rate controls. We used a 30% contingency factor to build such a system. Note that the model further assumes that several of these systems are built. We assume that once the first two systems are built at the cost given in Table 2, additional systems can be built for \$2000k each, taking away the engineering and contingency costs.

Each system described above with 3 shifts/365days and a 55% duty factor would produce 390 km per year of cm-wide equivalent tape. We assume a yield of 70% of this value for the final product. To bring the production to roughly 5000 km per annum we assume that 10 such deposition systems are required. We calculate the raw material expenses for 10 deposition systems as shown in Table 3. Deposition efficiency is assumed to be 10%, as stated above, with no recycling of materials assumed. Table 3 shows the amount of material used and the annual cost assuming the prices of 99% purity materials to be \$50/kg for Cu, \$200/kg for Ba, and \$350/kg for Y.

Labor costs are based on three shifts of 5 operators and a shift manager in each shift, and a half time of a site engineer. Accounting for a 50% in additional indirect staff, and loading the labor fully, we estimate the total labor cost at \$1600k. Capital expense for the equipment is depreciated over 8 years. Additional indirect costs are added for another 50% to include building, utilities and the like. We believe that all these estimates are very conservative.

TABLE I
PROCESS PARAMETER ASSUMPTIONS IN THE SCALED UP
MODEL OF RCE WITH A DRUM HEATER.

Drum diameter (cm)	45
Circumference (cm)	141
Total width of tapes (cm)	100
Drum rotation speed (Hz)	2
Deposition zone width (cm)	15
Deposition zone length (cm)	100
Deposit per revolution (nm)	0.4
Deposition rate (nm/s)	7.5
Deposit per tape pass through (μm)	2
Individual tape speed (cm/s)	0.04
Combined effective speed (cm-m/h)	144

TABLE II
CAPITAL EXPENSES FOR A SINGLE DEPOSITION SYSTEM IN
THE RCE COST MODEL.

Capital Expenses	k\$
Chamber, pumps, vacuum controls	600
Evaporation source, hearths	850
Rate controls	400
Tape creel/heater	500
Contingency	700
TOTAL	3050

TABLE III
RAW MATERIAL EXPENSES FOR FOUR DEPOSITION SYSTEMS.

Raw material expenses	Annual cost (k\$)
Evaporation source Y: 2130 kg	746
Evaporation source Ba: 6407 kg	1281
Evaporation source Cu: 4472 kg	224
Gases, supplies	600
Total cost	2851

TABLE IV
TOTAL OPERATING EXPENSES FOR 4 RCE SYSTEMS IN A
MANUFACTURING FACILITY.

Operating expenses	Annual cost (k\$)
Raw materials	2851
Labor	1600
Capex depreciation	2825
Indirect cost	3638
Total cost	10914

This total cost yields a cost per meter of cm-wide tape of \$2.25. As stated earlier, we assume that the 2 μm YBCO layer can carry 500 A/cm, something that has been demonstrated in the laboratory, but which would also need to be proven in a scaled up production environment.

On the other hand, we also believe that there is additional room for further improvements in performance. The final cost given the assumptions presented here is \$4.50/kA•m. This cost is for the HTS layer deposition only, but includes indirect costs and yields which are factored in.

6. DISCUSSION

For the cost model presented here, we chose a certain size for the deposition system that has not been optimized. The design optimization is an iterative process in which many design factors enter, but most importantly economics of the process. Additionally, other issues such as the size of the deposition area, efficiency, etc., need to be optimized and would affect the cost numbers significantly. However, the resulting cost will never be more than a factor of 2 away from the cost given here, for the given size of production.

We believe that our cost model makes this RCE process attractive for manufacturing, since a total cost of coated conductor below \$10/kA•m appears to be achievable. We expect the metal tape and the template layer to be less expensive than the HTS layer. Our cost models indicate that the total costs for the metal substrate, substrate finishing, IBAD template, buffer layer, normal layer, and slitting are in total comparable to the HTS deposition cost.

7. CONCLUSIONS

The Garching implementation of the RCE process has been shown by several groups to be viable for fabricating coated conductors. We have demonstrated that high- J_c YBCO can be grown in a rotating heater with an oxygen pocket. The highest I_c achieved to date is 590 A/cm-width, and the highest J_c in a 1 μm thick film is 2.8 A/cm². The technique can be extended to utilize reel-to-reel transport in a very compact manner. A cost model for RCE manufacturing estimates that the HTS deposition cost can be less than \$5/kA•m.

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