Optimum Design of Copper Stabilizer on Coated Conductors

U. Floegel-Delor, T. Riedel, P. Schirrmeister, D. Wippich, R. Rothfeld, R. Koenig, F. N. Werfel

***Abstract*— Metallic copper is the obvious engineering stabilizing partner for the second generation coated conductor (CC) wire. The copper shunt on the conductor gives a number of electric, thermal and mechanical advantages. Non-vacuum deposition of copper by electrochemical plating is now an established CC technology, both single sided as well as surrounded. Cu plating on RABITS Ag/YBCO/Ni5%W and IBAD Ag/YBCO/YSZ /Hastelloy conductors are reported in the applied cell potentials, currents and coulombs. The diffusion – limited plating current in copper sulphate and alkaline electrolyte is investigated in view of the largest rate of mass transfer. The electrochemical deposition opens a further window of design and conductor engineering. Beneficial Cu plating with Ag cap layer is performed and Jc evaluated. All parameters are transferred into the REEL technique to improve the efficiency of copper plating. The paper describes the optimum and merits of Cu shunt parameters in geometry, thickness, and wire robustness.**

***Index Terms*—Coated conductor, copper stabilizer, electro-chemical deposition, reel-to reel plating.**

I. Introduction

TODAY'S SECOND generation (2G) coated conductors need a metallic stabilizer as partner to fulfill the technical requirements. Not surprisingly, metallic copper has been selected to protect the sensitive thin film layers of buffer and HTS. Copper plating is a convenient method to deposit metallic copper in a thickness of 10 to 100 µm on top of the processed coated conductor. Except the electric shunt function the copper stabilizer improves the mechanical properties of the tape and the thermal interface conditions. After the first experiments 15 years ago by covering YBCO bulk superconductors with copper [1] the observations of the surface show a clear copper diffusion process combined with a hardening of the copper surface layer.

Not surprisingly, the copper plating technique has been transferred into the 2G wire fabrication processes [2]-[4]. Three principle arguments hold for the copper plating technique and the results described in the present paper: (i) The non -vacuum technique is relatively easy to perform and economically relative to other 2G fabrication steps, (ii) Copper possess a peculiar chemical and physical significance in all high–T_c superconductors; it causes no degradation in the electric properties, (iii) Copper surface plating can easily transferred into a continuous reel-to-reel technique with speeds up to 100 m/hour.

Besides the electric shunt function the Cu matrix especially in surround geometry offers more advantages on the way to routine 2G applications like cables or windings for electric machines. The design of the shunt has been less studied but can form in different geometries on the surface of the HTS conductor.

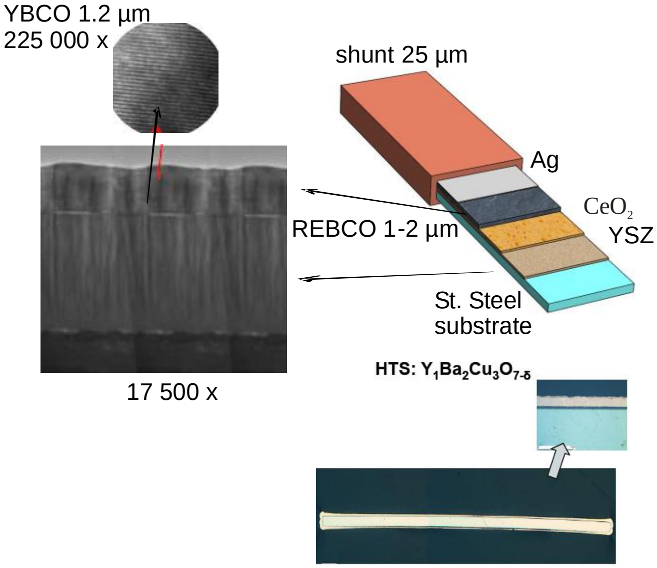

Fig. 1. YBCO architecture of Bruker's HTS coated conductor PLD fabrication;

With the one-side or surrounded copper layer the 2G wires have shown excellent current densities of 200-500 A/cm width (77 K, self – field). Electric contacts of extremely low resistance ($< 10^{-8}$ ohm•cm²) capable to feed the currents into the wire are now easier to realize. Although efficient superconducting joint of 10^{-10} ohm or less to enable a persistent current flow as in LTS coils of MRI systems is presently not seen, HTS high-current contacts are essential for all applications.

At present most of the 2G wire developing and fabricating companies [5]-[6] use Cu plating technique as it is shown in Fig. 1. Among plated copper layer other forms like Cu lamination for high current application is an alternative shunt technology. We will investigate and analyze the parameters and functions of copper plating technique reported already [7]-[8]. The variation in the shunt design development is

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Manuscript received August 12, 2014

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presented and the improved mechanical properties of 2G wires with Cu shunt demonstrated.

II. EXPERIMENTAL APPROACH

A. *Electrochemical basics of Cu deposition*

Electrochemical deposition has been found to be the most efficient method to date to deposit metallic copper on the surface of 2G coated conductors (CC). In a microscopic picture is the deposition started of a first ultra-thin adhesive Cu layer of a few nanometers and islands, followed by a seed layer with great advantage for a homogeneous flat structure. Pinching off of small surface inhomogeneities is avoided ensuring adequate sidewall coverage. The plating basics in the following steps were analyzed in a series of test samples shown in Fig. 2.

The charge transport is regulated by Faraday's law. The transferred mass m_{Cu} is proportional to the flowing current during a time with the proportional factor F known as the Faraday factor.

Fig. 2. Experiments of copper plating parameters on CC surfaces: Substrate Hastelloy and NiW, plating solution, current density, and pulse structure.

$$m_{\mathrm{Cu}} = F \bullet Q \qquad \text{with } Q = \int I \bullet dt \qquad (1)$$

The total charge is thereby integrated over the time. F is denoted as electrochemical equivalent. Alternative concurrent reactions at the electrodes influence the plating process. In aqueous solutions often a discharge of hydrogen may occur. This reduces the current efficiency CE of the metal transfer. The ratio $CE = Q_{\mathrm{metal}} / Q_{\mathrm{total}}$ gives then the efficiency of the galvanic process. For copper plating the theoretical copper mass plated on a 4 mm wide CC tape can be calculated. For the constructed copper plating unit shown later we assume the following parameters: 100 m length, 1 hour plating time, and 12 cells each with 3 Amperes continuous processing. If we assume 100% efficiency after the Faraday equation the transferred metallic copper into the solution is 42.7 g. If this mass is deposited completely on the 4 mm wide tape (considering half density of the surface copper one side) the obtained layer thickness is about 20 µm. A stabilizer Cu thickness of 20 µm is a commercial standard value, thus it remains beneficial as an electric shunt but is still flexible enough for winding purposes.

$$m = j\,t / (n\,F) = 3\ \mathrm{A} \times 12 \times 3600\ \mathrm{s} / (2 \times 96485\ \mathrm{As/mol}) \times 63{,}54\ \mathrm{g/mol} = 42{,}7\ \mathrm{g} \qquad (2)$$

Practically, to control the process the total plated mass is estimated by simple weighting the working copper electrode before and after the plating process. In the above approach we assumed a continuous plating process. The low electric conductivity of the coated conductor substrates at room temperature limits the current however that can be applied at a certain tape length.

B. *Pulse plating technique*

As an example, Nickel based Hastelloy possess a specific electric resistivity of 1.18 µΩm at room temperature. For a length of 1.2 m, 100 µm thickness and 4 mm width the total resistivity is 3.54 Ω. The power distributed along the tape follows with,

$$P = I^2 R \quad \text{current } 12 \times 3\ \mathrm{A} = 36\ \mathrm{A} \rightarrow \text{ power } P \sim 4.6\ \mathrm{kW} \qquad (3)$$

This high power would heat the Hastelloy tape in a very short time. In addition, the electric load shows a non-linear distribution. Pulse plating of the current is therefore recommended. The pulse current is either directed to cathode (unipolar) or bipolar pulses send to both the anode and cathode. Bipolar processing with a reverse current built periodic layers with special properties and improves the homogeneity of the current distribution. Pulse plating is characterized by a wide variety of current-time functions. The averaged current density j_{av} changes the time function to,

$$j_{av} = j_p\,[\,t_p/(t_p + t_0)] \qquad (4)$$

Typically a program is started with an initial pulse p_i with a short duration t_i. This pre-pulse generates a layer on the substrate surface with tiny seeds and because of the low current it prevents unwanted dendrite growths. Between the

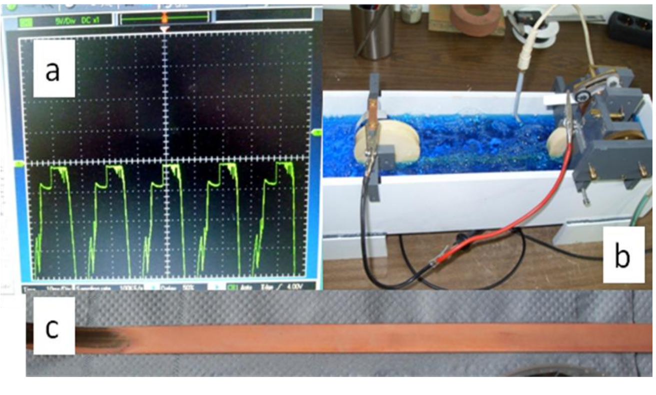

Fig. 3. Small-scale plating experiments of pulse current structure (a) and test solution chamber (b); ready processed 2G conductor with 35 µm Cu shunt (c).

pulses the actual surface can relax for producing a flat and homogeneous layer growth. Under circumstances pulse plating function is more complex consisting of a pre-pulse, further growing with a low-current pulse followed by a reverse anode current to removing peaks and spikes of the growing layer and finally the relaxation time. Fig. 3 gives a corresponding pulse current- time function of 10 ms pulses. The experiments were performed in a small reel-to-reel chamber by variation of the electrolytic solution (acid and alkaline), the temperature, electrolytic current density between 30 – 60 mA/cm² and the pulse-time structure. We investigated pulse current/zero current in time ratio 1: 1 up to 1: 3. The best Cu layers in seeding and growing a fine grain structure are obtained at a three times longer relaxation time relative to the pulse duration (1: 3). The chemical solution of $CuSO_4$ + H_2SO_4 has been investigated with 10 – 35 % sulfuric acid. The solution conductivity is measured to 130 mS/cm and increases the current density for deposition rate of 1.6 µm per minute at a current of 45 mA/cm². Comparable results for the alkaline solution are reduced to about 30 % of the copper sulfate process. The electrochemical deposited copper layer by alkaline electrolyte is more fine grained, dense with a more shiny color than the layer of the $CuSO_4$ route (Fig. 3).

Pulse plating PP of copper on HTS shows a number of advantages: (i) PP change the mass transport efficiency in the Nernst Diffusion barrier at the cathode in a positive way; the metal concentration at the cathode follows the pulse frequency and reduces the thickness of the diffusion layer. (ii) High current density of the pulses generates a seed density on the substrate that results in a fine grain structure. (iii) Pulse current plating drives the process to higher reaction kinetics. (iv) The reverse pulse is capable to remove metal from the surface, and causes a surface flattening, reduces the dendrite formation and changes the grain size of the layer.

C. *Reel-to-reel pulse plating apparatus*

For continuously electrochemical deposition a reel-to-reel technique and an experimental facility has been proposed and constructed [2] - [4]. The high tape resistivity of Hastelloy and Ni5%W tape discussed above prevents a continuous DC power on the conductor. In figure 4 a multi-cell electroplating unit for pulse operation and long- length processing is shown [3]. The apparatus possess 12 neighboring galvanic cells of the dimension 100 x 100 mm² with through slits for transporting the tape. Each cell has its own pulse power supply with maximum current of 3 A. The power supplies are connected and controlled by a computer in a master-slave operation process. The plating infrastructure of the unit allows free programming of the pulse power sequence. Typically, three plating cells are combined to one group which is energized simultaneously (Fig. 5). However, the three member cells of one group are homogeneously distributed over the total processing length of 1.2 m. This distribution prevents an electric overload of the tape. Next the second group is energized and the first group is switched off (see schematics Fig. 4). The operation sequence improves the plating efficiency and protects the tape during the electrochemical Cu deposition.

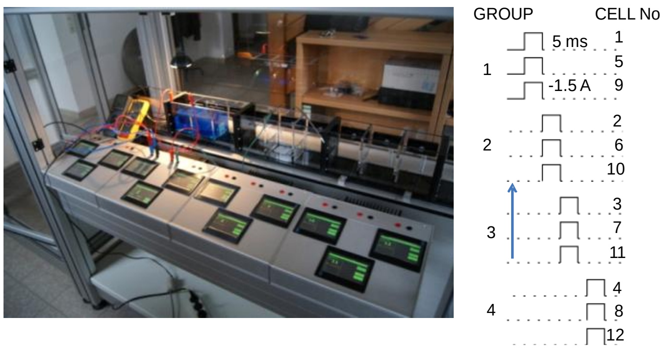

Fig. 4. Reel-to-reel copper plating unit for processing long- length coated conductors; pulse current and power sequence operation with distributed electric load (right).

III. RESULTS AND DISCUSSION

A. *Shunt design*

The present development of 2G wires is determined by the application. The most important parameter of a conductor is the engineering current $j_e = j_c / (w_{ins} \, x \, t_{ins})$ with j_c the critical current density at self field. w_{ins} and t_{ins} are the geometrical dimensions of the width and thickness of the insulation. The thickness t_{ins} summarize thereby the buffer and insulating layer of the conductor. For components of electric machines like coil windings of motors a high engineering current density is desirable (e. g. 250 A/mm²). Other applications like large generators or transformers need high total current, cable applications benefit from a high current per conductor width.

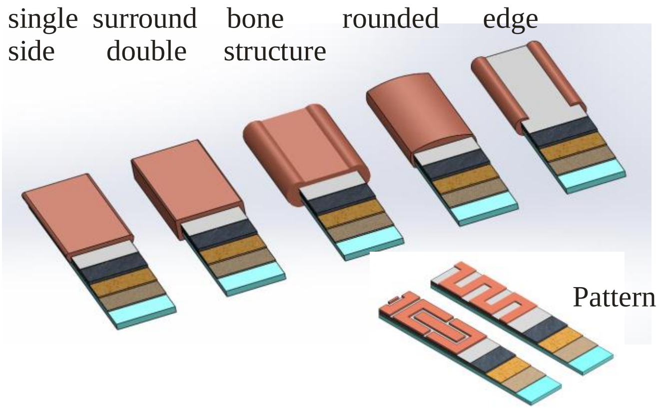

Fig. 5. Copper shunt structure ranging from single side to edge bone structure plated using preferential deposition.

The size and shape of the copper layer influences the wire properties and the application. The present aspect ratio width to height is far from being at optimum (w/t = 4000 µm/130 µm ~ 30: 1). If the substrate tape thickness is 50 µm only or the width is increased to 12 000 µm the aspect ratio is becoming close to 100: 1. From technical skills of application circular conductor geometry shall be deemed to be at best. An aspect ratio of 3: 1 is still adequate for many assembling processes.

The aspect ratio of the present coated conductors can be shifted by copper shunt deposition. In the experiments of figure 1 and 2 the Cu layer thickness obtained by electroplating is typically 20 µm on both sides. It can be increased to higher layer thickness of 50 – 60 µm and reduces the aspect ratio. The shunt thickening is a special performance merit in case of high current applications. Here the copper matrix stabilizes the conductor better against hot spots, short currents, and cryogenic fluctuation.

Fig. 5 displays different Cu matrix geometries above the conductor proved in experiments. One-side and surrounded copper belongs to the standard design of CC fabrication. The bone structure is an effect of the electroplating process because of the preferential high electrolytic field at the tape edges and the more effective mass transport to the edges. As shown in Fig. 1 in the micrograph the “bone” thickening at the tape edge amounts to about 20 % relative to the tape center but can be stronger. A reverse effect is obtained by shielding the edges during the plating process and position the Cu anode during the galvanic process parallel to the tape center. The shielded electrolytic field in the galvanic cell then transports Cu atoms preferentially to the tape center yielding a center surrounding effect as schematically given in Fig. 4. Finally, a discrete edge Cu deposition improves the high – voltage and insulation stability and limits the losses, especially the AC losses. Patterned structure in the lower part of Fig. 4 goes in the same direction. It establishes the shunt function but limits losses and hysteresis effect.

B. Performance merits on CC through copper shunt

With combination of copper the 2G wires achieve a number of performance merits and advantages. The copper matrix around the conductor gives improvements in design, electric and thermal properties. Independent on the electric and current transport capabilities the new generation of 2G conductors with increased application field are evaluated with respect to the mechanical properties and the handling robustness (Fig. 6 and 7). The maximum tensile strength of CC in Fig. 7 has been shifted to 550 MPa without degradation of j_e. In Fig. 6 the conductor with Cu shunt shows a smaller bending radius of 6 mm at full I_c compared to a value of 10-12 mm without Cu shunt. The Cu shunt is especially valuable under insulation and winding conditions perpendicular to the conductor plane (“high edge winding”). The above discussed high aspect ratio causes severe problems by electric insulating the heads of generator or motor windings. The edges and slits of conductor windings are the critical places where high – voltage spark-over often occur.

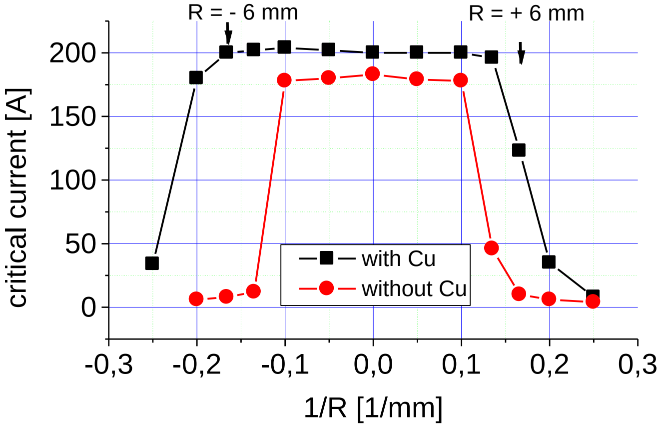

Fig. 6. Measurement of the J_c dependence on the bending radius; the PLD CC wire with Cu has a significant smaller bending radius.

Full real-sized high current/high field measurements are performed with thick Cu shunt. [4]. At a copper plating thickness of 2 x 45 µm on both sides of a Bruker PLD - tape at a Helium temperature of 4.2 K very high currents of 1000 A at 6 T and 500 A at 16 T (B||c) could be obtained. The thick copper layers demonstrate two merits. First, the electric shunt function bridges the high current at eventually weak-link/ grain boundaries in the textured YBCO layer. Secondly, the measurements have shown the gas – tightness and protection capability of the copper layer against the helium bath.

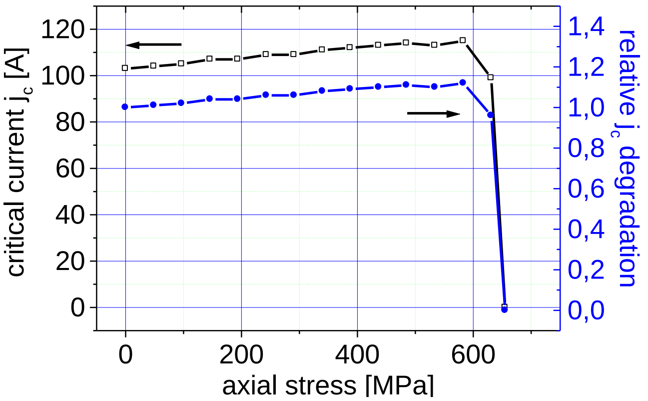

Fig. 7. J_c measurement of PLD conductor under axial stress conditions up to an axial stress of 650 MPa.

IV. CONCLUSIONS

The present coated conductor design has deficits (aspect ratio 30 - 60, short-current sensitivity, high -voltage insulation, difficult edge winding capability and voltage insulation) A copper stabilizer on the surface as an additional metal matrix improves electrical, thermal and mechanical properties of CC. Geometrically variable Cu layer design in parallel shunt function or patterned is processed using plating technique.
Non-vacuum pulse current plating process is now established to contribute and finish commercial coated conductor products.

ACKNOWLEDGMENT

We gratefully acknowledge and thank Alexander Usoskin, Bruker HTS for the cooperation and discussion to integrate copper plating routinely into the 2G development.

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