Copper – HTS Hybrid Conductor Architecture

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Abstract. Plating of a copper layer using an aqueous copper sulfate electrolytic deposition on the surface of CC is described. The paper focuses on basic electrical and chemical parameters. High concentration copper sulfate solution of 150 – 250 g/l with low content of sulfur acid solution at electrolytic current densities of 30 – 50 mA/cm² delivers fine grained stable Cu layers. A noble metal (Ag, Au) seed layer improves the deposition speed and the tape surround plating. Pulse plating increases the plating efficiency and is utilized in a developed reel – to – reel plating unit to deposit a Cu shunt on CC continuously. Mixed electrolytic solutions are the electrochemical basis for CuNi and brass deposition. Practical solder joints are obtained using Sn-Pb-Cu standard soldering at temperature of 250 °C. A joint resistance of 0.2µΩcm² could be obtained routinely in practical CC assembling.

1. Introduction

Copper electroplating is a key technology to deposit an electrical Cu shunt on the surface stabilizing the conductor against electric and thermal overloads and fluctuations. In addition, copper plating technique is a very effective and inexpensive non-vacuum method. It has been successfully used over more than one decade to metallise HTS bulk material [1]. Several patents are issued and granted [2]. In the paper the influence of the copper layer on the PLD YBCO conductor architecture is investigated. Optimum method parameters and obtained results of a reel- to- reel plating unit are reported. Improved electric and mechanical conductor properties together with reel-to-reel operation and cost efficiency of the Cu plating method are expected to boost the coated conductor production and application. While previous Cu plating on HTS was performed in limited dimensions the fast growing REBCO second - generation (2G) HTS wire fabrication with long length requires a suitable continuous reel -to- reel copper plating technology in long length. Presently the most advanced and prominent producers of 2G coated conductors (SuperPower, AMSC, Bruker HTS, Fujikura) use copper plating or Cu laminating in the CC fabrication procedure. The copper - HTS combination provides a robust and ready -to - apply engineering conductor. Recently the influence of a copper shunt on electrical and mechanical properties of coated conductors of second generation is investigated carefully [3].

The major advantage of this type of deposition is the peculiarity and the unique position of the element copper as the chemical and structural carrier of all new HTS materials with $T_c > 80$ K. Because of the physical and chemical affinity of copper and copper alloyed layers between surfaces and interfaces the plating layer shows strong bonding metal – HTS properties, especially in the long – time behavior. The functional properties and advances of a copper layer on the CC surface are shown in Fig.1 schematically.
The deposition method of metallic copper on HTS is utilized for the fabrication of electrical, thermal or optical contacts. The here described Cu plating deposition technology is a non–vacuum, easy to perform, fast and economical procedure.

2. Conductor fabrication

Different technologies and methods have been developed for the HTS thin film epitaxial formation on textured surfaces. The texture is generated using ion – beam assisted deposition (IBAD) or rolling-assisted biaxially textured substrates (RABITS).

The coated conductor technology of Bruker HTS [4] is based on 100 µm Cr – Ni stainless steel tape which is carefully mechanically polished. An IBAD technique is followed for the deposition of yttria-stabilized ZrO₂ (YSZ) as buffer layers. In - plane alignment values of about 8° are achieved. It follows a 50 nm thin CeO₂ layer before the YBCO film is processed by high – rate pulsed laser deposition (HR- PLD). The film thickness is varied between 0.5 and 1.5 µm. The final step is non -vacuum copper plating directly onto the YBCO or via 0.2 µm Ag cap or seed layer. The principal CC fabrication steps of Bruker HTS are shown in Fig. 2 by the tape status.

A comparable PLD technology of the coated conductor fabrication is developed and processed by Fujikura, JP. Different ways and methods are followed in the US. SuperPower Inc. developed an efficient REBCO /BZO metal organic chemical vapour deposition method (MOCVD) with MgO IBAD technique achieving presently conductor length’s of more than 1 km with Jc above 280 A/cm [5]. Summarizing the reports all industrial producers deposit a copper shunt on the conductor surface or laminate a metallic / Cu sheet (AMSC, USA).

3. Plating method

3.1 Cu plating

Copper plating can be performed either in an acidic or an alkaline electrochemical process. There are several fundamental issues need to be addressed before copper plating on CC. The electrolytic deposition of copper on high temperature superconductors is most effective in a copper sulfur acid solution CuSO₄ x 5 H₂O as electrolytic solvent by applying high current density. Furthermore, copper can be deposited to use an electrolytic bath of alkaline copper cyanide. The cyanide process needs however extreme care in process and handling conditions because of the strong toxic solvents.

Referring to Fig. 3 a preferred electrolytic cell with the Cu anode and the HTS cathode is operated by a DC source providing the electrolytic process. On this basis a copper plating reel–reel unit has been developed and tested for long length conductors. The plating unit is shown in Fig. 4.

The current source is assembled for low HTS cathode conductivity and allows the current flow constant, reverse or in a wide ratio of pulse plating. The period and time ratio between positive current, zero and negative current is variable in a range from 0.1 Hz (10 s) to 100 Hz (10 ms). Due to
pulse plating applied a higher electrolytic current density enables substantial faster deposition. The layers become fine grained and are mechanically stable bonded on the CC surface.

A number of aspects are correlated with the speed of the electrochemical reaction in the bath. Basically is the speed of reaction in the Cu plating process a function of the applied voltage. Practically the voltages depend on the geometrical factors of the galvanic cell and were found to be between 1.8 – 4 Volts. As more negative the cathode is as stronger the reaction rate. Finally, the Cu²⁺ concentration profile must adjust to match the mass transfer and reaction rate. Typical values of the electrolytic composition for fine grained Cu plating are given in table I.

For effective plating process the electrolytic solution is moved in a circular process in permanence or periodically to remove impurities and to prevent sticking of reaction products on the HTS surface especially under high electrolytic current densities.

The concentration of sulfuric acid H₂SO₄ has be as low as possible in case of plating directly onto the REBCO surface. Deposition on a metallic cap layer of Ag or Au allows higher sulfuric acid concentration in the electrolytic solution up to 30 g/l. With increasing sulfuric acid the conductivity of the electrolyte solution increases too. In contradiction, a high copper sulfate concentration reduces the bath conductivity.

Advantages

- Aqueous- based process, Cu sulphate solution;
- No or less sulphuric acid
- Atmospheric pressure
- Current controlled deposit
- Continuous or pulse current
- Composition selected deposit via potentials
- High selectivity
- Scale- able processes, industrial level
- Low cost
- High rate deposition
- Robust technique
- No HTS degradation

Copper plating can be deposited electrochemically directly on the REBCO surface. Thereby the room temperature conductivity of the HTS layer of a few mΩcm allows direct surface plating. Alternately, a thin metallic seed layer of noble metals (Ag, Au) of 0.1 – 0.5 µm thickness improves the electrolytic current density and provides the capability of plating on both sides of the tape.

After electroplating the plated CC is heated at moderate temperatures of 100 – 150°C to accelerate the Cu interdiffusion between tape and shunt. This improves the bonding strength of the copper shunt.

### 3.2 Cu alloy plating

Not only metallic Cu using a electrochemical process can be plated but also Cu alloys. Prominent copper alloy materials are the compositions CuZn (brass) or CuNi. The plating here is performed with mixed solutions using an electrochemical process with a citrate –like electrolytic solution.

After electroplating the plated CC is heated at moderate temperatures of 100 – 150°C to accelerate the Cu interdiffusion between tape and shunt. This improves the bonding strength of the copper shunt.

| CuSO₄ x 5 xH₂O | 150 – 250 g/l |
|----------------|--------------|
| H₂SO₄          | 0–35 g/l     |
| Temperature    | 20 – 40°C    |
| Current density| 30 – 50 mA/cm²|
| Voltage per cell| 1.8 – 4.4 V |
In a similar process the alkaline route of brass deposition uses 0.1n copper cyanide and 0.1 Zinc cyanide. The current potential curves of Cu and Zn are close together by 0.2 V at a current density of 0.1 – 0.3 A/dm². The potential curves are ideally situated to deposit a homogeneous brass layer on CC surfaces. In some cases Cu and the alloy partner are electroplated separately and after that the alloying is performed by annealing at temperatures between 300 and 600° Celsius.

Table II: Cu-Ni mixed electrolyte

| Electrolyte         | Concentration |
|---------------------|---------------|
| Copper sulphate CuSO₄ x 5 H₂O | 5 - 20 g/l |
| Nickel sulphate NiSO₄ x 7 H₂O | 30 – 100 g/l |
| Lemon acid C₆H₈O₇ x H₂O | 80 – 100 g/l |
| Sodium chloride NaCl | 3 - 5 g/l |

A further advantage of metallic plating is the additional mechanical stabilization of the superconductor provided by the deposition of brass CuZn or CuNi on the surface of CC.

4. Soldering of low resistance joint

The deposition of a copper layer on the coated conductor surface provides not only a high electrical stability of the conductor but also an easy soldering technique to connect two or more conductors. The procedure is ultimate for winding and assembling coils or coil structures.

Contact resistivity is expressed typically in terms of a specific resistivity ρᵥ of the obtained contact:

\[
ρᵥ = \frac{R \cdot A}{L} \quad \text{with}
\]

\[
R = \text{contact resistance} \quad [\Omega] \quad A = \text{contact area} \quad [\text{cm}^2]
\]

With the definition above the interface quality can be described by a quantitative parameter which is independent of the contact area.

The contact quality and the interface resistivity contribution depend on the contact materials used. Thereby the contribution of a few μm thick interface layers of noble metals and Cu to the overall contact resistivity is not a problem. In contrast, the contribution of soldered layer can be more significant: A 10 μm thickness Cu layer at 77 K with \( ρ_{\text{Cu, 77K}} = 0.2 \, \mu\Omega\text{cm} \) gives a specific resistivity of \( 2 \times 10^{-10} \, \Omega\text{cm}² \) as interface contribution to the total resistivity while a 0.1 mm thick SnPbAg solder with \( ρ_{\text{SnPbAg, 77K}} = 4.45 \, \mu\Omega\text{cm} \) results finally in a \( ρᵥ \) value of \( 4.5 \times 10^{-8} \, \Omega\text{cm}² \). Clearly the latter is two decades higher than the Cu layer itself (Fig. 5).

However, the selected material of the interface is only one step to the contact fabrication. The widely used noble
materials Ag and Au are chemically strange to the oxide superconductors. Both metals show a considerable interdiffusion under high – temperature annealing of about 500°C forming the noble metal layer. Very low diffusion joint resistance values of $10^{-8}$ Ωcm² are reported [6] but the problem of attaching leads or current bus bars on the noble metal buffer layer remains.

We tested different joining methods by soldering low melting Bi and In solder at 120 – 180°C. Best results under practical conditions (RT, normal atmosphere) were obtained using standard Sn60Pb38Cu2 solder at a soldering temperature of 250 – 270°C. Soldering was performed on the YBCO side without observing any degradation in the superconducting properties. The measured joint resistance of the soldered connection in Fig. 6 at 77 K was $\rho_c = 200$ nΩcm².

5. Conclusions

Electroplating of a Cu shunt improves the performance of coated conductors substantially. The method originally was developed for contacting purpose of HTS bulk material. It but has been successfully transferred to coated conductor technology. The plating parameters are estimated to be efficient to deposit hard bonded Cu layers of 20 – 30 µm on CC surfaces. The method uses aqueous copper sulfate solution CuSO₄ in high concentration as electrolyte at electrolytic current densities up to 50 mA/cm². A reel -to-reel plating unit has been developed, constructed, improved and updated within the last two years. Soldered joints at HTS – Cu hybrid conductors show specific joint resistance values of 0.2 µΩcm² indicating promising low losses in case of coil connections and operation.

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