Electrodeposition of Silver Gold Alloys on $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ Ceramics

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Abstract—A metallic coating on the surface of bulk high temperature superconductors (HTS) is a promising alternative in order to increase the HTS stability for large scale applications. The coating provides an evacuation path for the heat generated by hot spots within the HTS, which improves their thermal stability. This is even more evident in thick films geometries, which are frequently used in fault current limiters.

In this paper, silver-gold alloys have been deposited on 1.8 mm in diameter Bi-2212 textured bars using an electrodeposition technique in non-aqueous solvents. The deposition parameters have been adjusted to obtain a coating of different alloys with gold contents in the range 0–5 at % and with a thickness up to 45 μm . Electrical and thermal measurements have been performed. The results show the possibility of controlling the thermal and electrical conductivities of the composite material by adjusting the layer thickness and composition of the metallic coating.

Index Terms—Bi-2212, coatings, electrodeposition.

I. INTRODUCTION

BULK high temperature superconductors, and in particular $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (Bi-2212) materials, have been used in some high power applications as hybrid current leads [1], [2] or fault current limiters [3]. To improve the performance of these materials, in some cases it is convenient to deposit a metallic layer on their surface. An initial objective of this layer is the protection of the superconductor against environmental degradation and to improve the stability. This layer also provides electrical and thermal conducting material to dissipate heat and provide a parallel conducting path for electrical current. This metallic layer determines the final thermal properties of the composite because the superconducting material shows a very low thermal conductivity values.

In this context it is important to have a reliable and inexpensive method that could control the electrical and thermal properties of the composite sample. Electrodeposition is an adequate procedure to obtain this metallic layer [4]–[7]. Depositions from aqueous solvents on copper high temperature superconductors using the oxide as cathode lead to a deterioration of the surface due to the strong chemical interaction of the superconducting material with water. For this reason it is necessary to

TABLE I
SAMPLES CHARACTERISTICS

	Metallic coating composition	Sample diameter	Metallic coating thickness before annealing	Metallic coating thickness after annealing
S0	Uncoated	1.84 mm	- -	- -
S1	Ag	1.86 mm	23 μm	19 μm
S2	Ag-0.4 at% Au	1.88 mm	23 μm	21 μm
S3	Ag-1.9 at % Au	1.80 mm	53 μm	45 μm
S4	Ag-5 at% Au	1.80 mm	53 μm	45 μm

use non-aqueous media, such as acetonitrile, methanol, propylene carbonate [4]–[6] or dimethylsulfoxide [7].

One peculiarity of technological high temperature superconductors is their peculiar mixed-valence chemistry and their redox behavior. For this reason, only a few metals are stable with superconducting oxides. Silver is the most frequently used material but it has a very high thermal conductivity which is not adequate in some applications. Other alternatives as copper [4], [8], lead [5] and tin [4] have also been studied.

A similar problem appeared in $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ tapes. In this case several silver alloys were studied. In addition to the previously mentioned problems, harder sheaths than silver were required. The most frequently used alloys were gold and magnesium ones [9]–[12]. The AgAu alloys show thermal conductivity values higher than the AgMg ones, in the range 20–200 W/m K for temperatures between 10–100 K [9], [11].

In this paper, using electrodeposition we have succeeded in depositing several silver-gold alloys on Bi-2212 rods with different thicknesses and compositions. The objective is to control the electrical and thermal conductivities of the final rods and increase the technological applications of these bulk high temperature superconductors.

II. ELECTRODEPOSITION PROCEDURE

Metallic coatings have been deposited on Bi-2212 thin rods with approximately 1.8 mm in diameter (see Table I). These samples were textured using the laser floating zone technique. The samples were fabricated using a Nd-YAG laser with a growth rate of 35 mm/h. Typical critical current density values at 77 K are 3000 A/cm². After the texturing process the Bi-2212 phase is not the main one and a two steps thermal annealing is required [13]: the first one at 870 °C in order to form the Bi-2212 phase by diffusion and the second one at 801 °C to adjust the oxygen content.

The electrodeposition process is performed before the thermal annealing [7]. A simple current source device with two electrode setup was used for the electrodeposition experiments, the superconducting rod being the cathode and a sacrificial

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metal coil the anode. Silver electroplating was carried out using a solution of 0.5 M of AgNO_3 and 20 mM of thiourea in dimethylsulfoxide (DMSO). Typical electrodeposition parameters were 10 mA, 18 min for a 20 μm thick, 1 cm long contact. Longer contacts were obtained using intensity values proportional to the contact length while thicker contacts were produced increasing the electrodeposition time. Gold electroplating was carried out using a solution 0.1 M of HAuCl_4 and 20 mM of thiourea in DMSO. Electrodeposition parameters varied in the same way as explained for silver, using as reference 3 mA for a 1 cm long contact. The time for each experiment was calculated to produce the desired %Au on the already deposited silver layer. For instance, for a 5 at%Au on Ag alloy in a 20 μm layer, a 9 min deposition time was necessary. It is important to note that Au(III) oxidizes the silver layer producing metal exchange, so electric potential was applied to the electrodes previously to their immersion in the electrolyte to minimize this redox reaction.

Fig. 1(a) shows the aspect of a metallic layer before annealing. In this case, silver was the first component to be deposited and we can observe a silver layer, 10 μm thick, on top of the superconductor (lower region in the photograph with two grey contrast). On the upper part of the photograph we can observe the gold layer. There is an initial 2 μm thick layer with a gold layer on top of a silver one and finally, in the top of the photograph, more irregular gold growths.

After annealing (Fig. 1(b)) the aspect of the layer is more uniform and the gold is almost uniformly distributed in all the layers. Usually, the gold content is near a 15% below the predicted value. In this process the layer also densifies and the thickness decreases.

For this work, four coated samples have been analysed, two with a metallic layer of around 20 μm and the other two with a thickness of around 45 μm . The exact composition and thicknesses before and after annealing that have been obtained in the four metallic coatings are presented in Table I.

III. THERMAL AND ELECTRICAL CHARACTERIZATION

A. Characterization Techniques

The thermal conductivity of the bars was determined with a commercial setup from Termis Ltd., using a longitudinal steady-state method. Specimens of 1 to 1.5 cm in length were measured. During the process, each sample is placed between two copper blocks with independent heaters, which can produce a thermal gradient across the sample. Under vacuum and with radiation losses minimized by a lateral shield, measurements of thermal flow and temperature differences are carried out. Once a stationary state is reached, the thermal conductance (K) is calculated from the ratio of the additional heat power supplied by the hotter block and the achieved temperature difference between both ends of the sample. Finally, the thermal conductivity, κ , is obtained from the expression $\kappa = K \cdot L/A$, where L and A are the length and cross-section of the sample, respectively. Further details of the set-up, measuring process and data treatment are described in [14].

Electrical measurements have been performed on 5 cm long samples using the four point configuration. Dc currents of 10

Fig. 1. Aspect of the metallic coating (a) before and (b) after the thermal annealing. Before annealing, the silver (close to the superconductor) and gold (white contrast in the top) layers are observed.

mA have been used in order to have enough sensitivity in the measurement of the coated samples.

B. Experiments and Discussion

The effective thermal conductivity, κ_{eff} , of the bars in the 45–150 K range, estimated using the length and cross-section of the whole composite sample, is shown in Fig. 2. The uncoated sample exhibits thermal conductivity values on the order of 2–2.7 $\text{W/m} \cdot \text{K}$ in the full range, with a small maximum around the critical temperature [14]. As expected, the metallic coating significantly enhances κ_{eff} . In particular, in the case of sample S1, an increase of one order of magnitude with respect to the uncovered bar has been obtained at 77 K with a 19-micron thick coating. Below 100 K, the thermal conductivity of

Fig. 2. Effective thermal conductivity of some samples with and without thermal coating.

Fig. 3. Calculated thermal conductivity of the metallic sheaths in some samples. Calculations have been obtained from the experimental data.

the sample increases when the temperature is reduced. This is in agreement with the maximum undergone by the thermal conductivity of pure silver at around 7 K [15]. Assuming that the composite is a cylindrical Bi-2212 bar with a uniform coating of 19 μm in thickness, the estimated thermal conductivity of the Ag coating at 150 K (far from the superconducting transition) is 504 W/m · K slightly higher than that of pure silver, 432 W/m · K [15]. Taking into consideration that the metallic layer thickness is not uniform and that the value of 19 μm is an average, this agreement is good enough indicating that a good densification of the silver is obtained during the thermal annealing.

The presence of an alloying element (Au) reduces the thermal conductivity of the coatings (Fig. 3) and, thus, κ_{eff} , as observed in Fig. 2. In effect, the introduced impurities and defects increase the scattering, which reduces significantly the electronic contribution to the thermal conductivity, lowering or even suppressing the maximum observed for pure metals, and shifting it to higher temperatures. In our case, an increase of a factor 3.3 and 4.8 in κ_{eff} with respect to the uncoated bar is still present for samples with Ag-5at% Au (S4) and Ag-0.4at% Au (S2) coatings, respectively (see Table II). No marked maxima are observed or expected at lower temperatures, since there is no increase of κ_{eff} below 80 K, and the small upturn around 100 K is mostly due to the normal/superconductor transition of the Bi-2212 core [16]. The comparison between samples S1 and S2 (pure Ag and the Ag-0.4at% Au) is straightforward, since their coatings are of the same thickness, but the Ag-5at% Au

TABLE II
COMPARISON OF THE THERMAL AND ELECTRICAL PROPERTIES OF THE COATED SAMPLES WITH RESPECT TO THE UNCOATED ONE, S0

	$\kappa_{\text{eff}}/\kappa_{\text{eff}S0}$ 150 K	κ metallic sheath 150 K	$\rho_{\text{eff}S0}/\rho_{\text{eff}}$ 300 K	ρ metallic sheath 300 K	T_c/T_{cS0}
S0	(2.6 W/m K)		(7.4 $\mu\Omega/\text{m}$)		(87.5 K)
S1	9.1	504 W/mK	24.9	18 n Ωm	0.96
S2	4.8	228 W/mK	19.5	26 n Ωm	0.96
S3	--	--	16.8	45 n Ωm	0.99
S4	3.3	69 W/mK	11.2	67 n Ωm	0.99

Fig. 4. Temperature dependence of the electrical resistivity in some samples. The left axis correspond to the uncoated sample S0 and the right one to the coated ones S1 and S2.

coating has a thickness approximately two times higher (45 microns). So, the κ of both alloys were estimated, and their values at 150 K are 228 and 69 W/m · K, for samples S2 and S4, respectively. Then the κ_{eff} for a Bi-2212 bar with a Ag-5%at Au coating of 20 μm would be 5.3 W/m · K and, therefore, twice the measured value in the uncoated sample. These results indicate that with a control of the electrodeposition process, the thickness and composition of the coating can be tuned in order to obtain the required effective thermal conductivity of the composite sample between values close to the superconductor thermal conductivity to values one order of magnitude higher.

The temperature dependence of the effective electrical resistivity is plotted in Fig. 4 and some data are compared in Table II. There is a small reduction in the critical temperature in the coated samples. During the initial step of the thermal annealing at 870°C the Bi-2212 phase is formed by diffusion and the metallic layer densifies. In the second step, at 801°C, the oxygen content is adjusted to the required value. This thermal annealing was optimized in uncoated samples [13] and obviously a dense metallic layer in the surface of the superconducting sample can modify the oxygen interchange processes that take place in the annealing.

The shape of the curve is also different. The uncoated sample shows the typical behavior with a linear dependence at temperatures above 125 K and a slope of 24 n $\Omega\text{m}/\text{K}$. In the case of the coated samples there is a sharper transition between the linear region and the superconducting transition. The slope of

this linear region is very similar in all the coated samples, $1 \text{ n}\Omega\text{m/K}$ showing very parallel curves at temperatures higher than 90 K.

Modeling the bar as two resistances in parallel and taking into account the approximations that are performed considering that the metallic layer thickness is uniform, it is possible to estimate the resistance of the metallic coatings. Table II shows these data at 300 K. The value of sample S0, that has a pure silver coating, are not far from the theoretical silver value $14.7 \text{ n}\Omega\text{m}$. In the case of the silver gold alloys, these resistivity values increase with gold content in a near linear way and indicates that the coatings are well diluted concentrations, at least for such low compositions.

IV. CONCLUSIONS

Electrodeposition is an alternative to deposit metallic coatings on high temperature bulk materials. With an adequate election of the thickness and composition of the metallic layer it is possible to tune the thermal and electrical conductivity of these materials.

Variations of one order of magnitude in κ_{eff} have been obtained. The thermal conductivity values range close to those of the superconducting material to close to those of pure silver. In the case of ρ_{eff} , variations are smaller and the obtained values with different gold contents are only two times higher than those obtained in the sample with a pure silver layer, in all the cases one order of magnitude higher than the values measured in the uncoated sample.

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