EDISON ACTIVITIES ON HTS AND MgB_2

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Abstract
This paper summarizes the main results obtained by Edison in the frame of its R&D activities in the field of High Temperature Superconductors (HTS) and the recently discovered MgB_2. Several processes are under development for their fabrication and the market penetration will be determined essentially by their cost and the exhibited electrical performances. Our efforts are focused on the continuous deposition of HTS layers on metallic substrates, by electrochemical and vacuum based technologies, and on the fabrication of MgB_2 manufacts, bulk and filaments, by liquid Mg infiltration.

1. Y-123 COATED CONDUCTORS

$YBa_2Cu_3O_{7-\delta}$ Coated Conductors (CC) have gained a great deal of attention thanks to their high critical current density, above 1 MA/cm^2 at 77 K, weakly dependent on magnetic fields. High current densities CC's have been demonstrated by many groups using Rolling Assisted Biaxially Textured Substrates (RABiTS) [1, 2] made of Ni and Ni-alloys. The intermediate deposition of a buffer layer is required to enable a textured growth of the YBCO layer and to prevent interdiffusion of metallic and spurious nickel oxide particles into the superconducting YBCO layer. Among the in-situ vacuum techniques, we selected the thermal co-evaporation process for its relatively low cost associated with its inherent capability to prepare high quality YBCO films uniformly over large areas [3] at relatively low temperatures below 700 °C.

Biaxially textured pure Ni and Ni-5at.%W alloy tapes have been employed as flexible metallic substrates. The tape fabrication and properties are described in detail elsewhere [4]. The 80 μm thick metallic tapes are characterized by a surface roughness better than 15 nm. To enable a continuous deposition, the vacuum chamber has been equipped with a reel-to-reel system (see figure 1) and with vibrating conveyors. The latter enable to refill in-situ the evaporation sources containing the different precursors. YBCO/CeO_2 layers have been grown as described in detail elsewhere [5, 6]. The continuous process consists of the following sequential steps: i) tape recrystallization and surface treatment, ii) 100 nm thick CeO_2 film deposition and iii) 0.5-2 μm

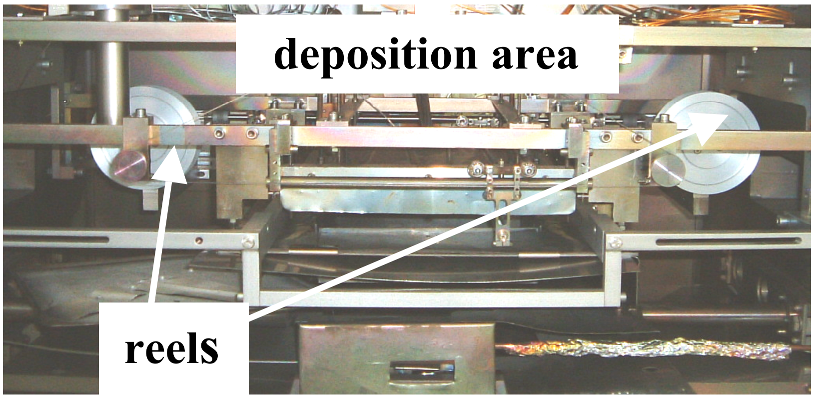

Fig 1. Reel-to-reel system for the continuous deposition of long length YBCO CC.

thick YBCO layer deposition. At the end of the process the chamber is backfilled with 500 mbar of oxygen and the samples cooled down to room temperature.

After recrystallization Ni tapes have been found to be full cubic {001}<100> biaxially textured with in-plane and out-of-plane full width half maximum (FWHM) values ≤ 8°. The degree of biaxial texture for both CeO_2 and YBCO layers have been studied. In figure 2(a) and 2(b) are reported the (111) CeO_2 and (113) YBCO layers pole figures, respectively. Typical in-plane and out-of-plane FWHM values are ≤ 6° for both CeO_2 and YBCO layers.

The morphological analysis are carried out by means of scanning electron microscopy (SEM). In figure 3(a) is shown typical smooth and crack free YBCO layer surface, which accounts for the excellent superconducting performances of the YBCO film. Cross section SEM image, depicted in figure 3(b), shows a very uniform and dense 1 μm thick YBCO layer

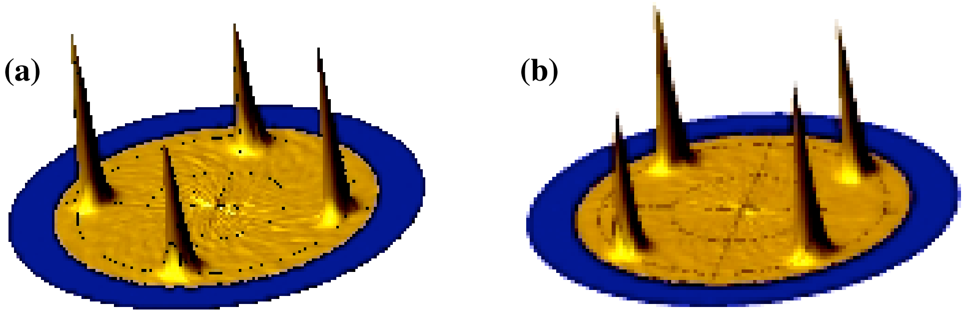

Fig. 2. (a) (111) CeO_2 peak and (b) (113) YBCO peak pole figures.

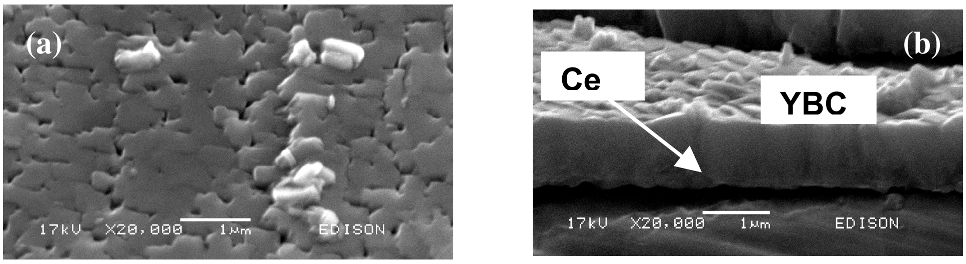

Fig. 3. (a) SEM picture of YBCO surface; (b) cross section of 1 μm thick YBCO film onto CeO_2 / Ni tape.

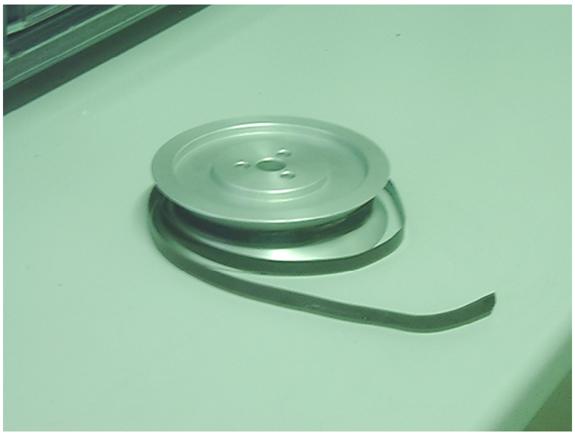

Fig. 4. 1 meter long YBCO coaterd conductor.

Remarkable critical current densities at 77 K, in the range 1-3 MA/cm^2 , have been obtained on 20 cm long YBCO CC by static and continuous deposition, suggesting that this route is scalable to an industrial process for the production of long coated conductors. Recently we succeeded to fabricate 1 meter long YBCO CC's (see Fig. 4). End-to-end critical current densities J_C of 0.6 μm thick YBCO, in the 1÷2 MA/cm^2 range, at 77 K self field, have been measured by transport measurements.

2. ELECTRODEPOSITED BI-2212

In the framework of the HTS coated tape activity EDISON is also studying a continuous process for the electrochemical deposition of Bi-2212 film on several meter long silver tapes. The process is based on sequential elemental depositions and alternate thermal treatments[7], see Figure 5.

The pilot plant to perform the BSCCO-2212 deposits on both sides of Ag tapes is built up through three main units, see Figure 6:

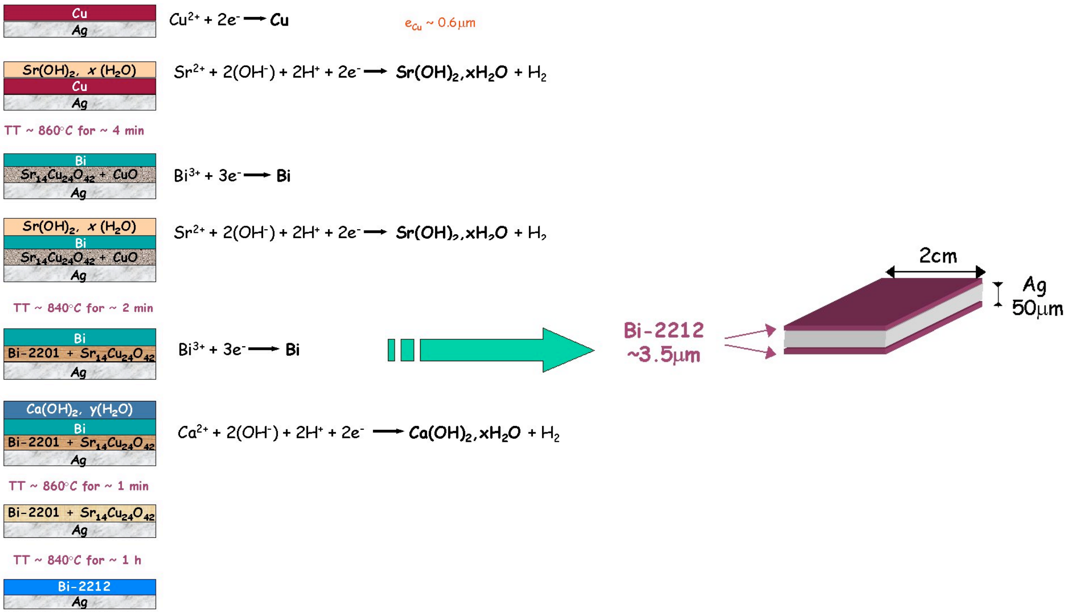

Fig. 5. The electrochemical process for Bi-2212 tapes.

a) the electrowinning copper section (Fig. 6a), in which the Ag tape (20mm wide and 50 μm thick) moves through a washing section, a coppering section and a final washing and drying section. (typical tape's speed of this section is 1m/minute);b) the modular Bi, Sr, Ca electrodeposition sections (Fig. 6b),that is followed by two washing section and a winding-on reel (typical tape's speed of this section is 30 cm/minute);

c) the heat treatments furnace (Fig. 6c), in which all the intermediate thermal treatments are performed passing the tape through a 5-stages tubular vertical oven with cooled heads (typical tape's speed of this section is 30 cm/minute).

The longer final heat treatment, of the order of 1 hour is made at the moment batch wise.

Fig. 6. Pilot plant for Bi-2212 : a) copper electrowinning ; b) Bi, Sr, Ca electrodeposition cells, c) furnace.

Starting from a 15 m long Ag tape we have produced several superconducting Bi-2212 tapes of good quality (some tens of cm long and 1 cm wide), see Figure 7. The Bi-2212 phase in small scale laboratory sample is very pure, in the pilot plant sample at the moment presents dark grains, due to the secondary phase, $(Sr,Ca)_{14}Cu_{24}O_{41}$, as detected by microanalysis. In Figure 8 the morphology of the deposited Bi-2212 film are displayed. In Figure 9 it is shown the electric field versus current density curve for a 20 cm long sample. The transport measurement is at 77 K in self-field.

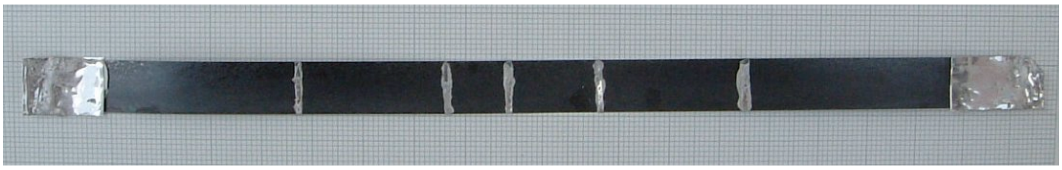

Fig. 7. A strip of the Bi-2212 coated tape , with voltage taps for transport V(I) measurement

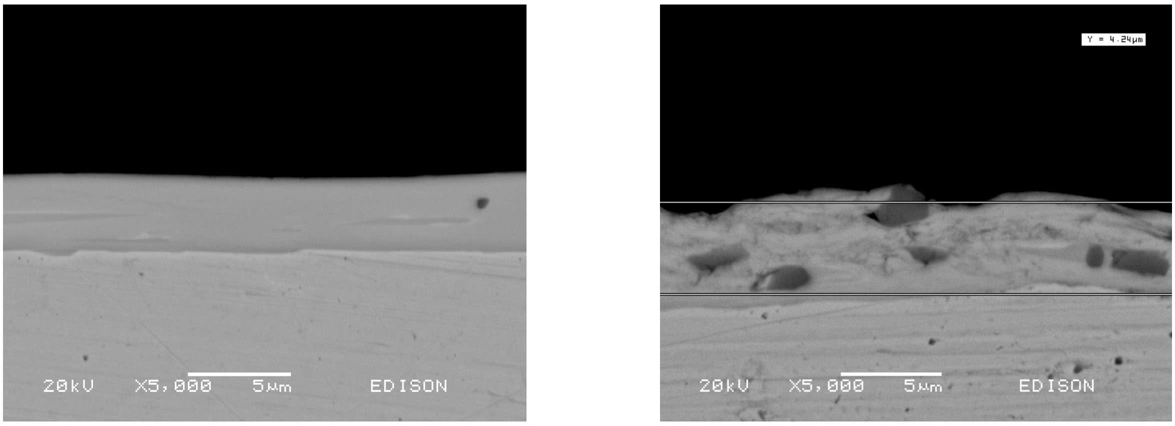

Fig. 8. SEM images (BSE mode) of cross section of the Bi-2212 deposit on the Ag tape : (left) good quality laboratory tape; (right) pilot plant tape.

The critical current density is larger than 20,000 Acm^2 and the n value of the interpolating power law is equals to 8.7. The critical current density value must be compared with the best values of 47,000 A/cm^2 obtained in the past by us at the laboratory scale with the same techniques, for very short samples, few cm long [8]. The key process variables to be controlled are: a) the uniform deposition of the elements on the tape, avoiding border effects; b) fine tuning of the annealing temperatures in a open vertical oven; c) assure constant electrolytic bath concentration during the time.

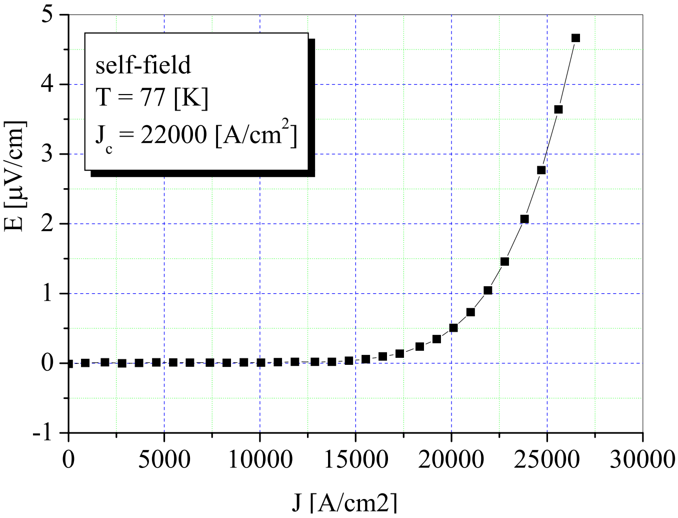

Fig. 9. Transport E(J) measurement on Bi--2212 electrodeposited tape.

3. MgB_2

Among the "in situ" techniques to produce MgB_2 manufacts, in EDISON we have developed a new technology, which we call the Reactive Liquid Infiltration (RLI) to describe the relevant aspects of process[9]. Indeed the liquid Mg infiltration in a powdery crystalline Boron preform, inside a closed container, is self driven by the pressure originated by the Mg volume increase at the melting point and is further aided by the Mg and crystalline B interface affinity, so that no external pressure is needed to reach very high homogeneity and high density, also when the permeation is several cm deep. This aspect represents the main advantage of the RLI technique that, in principle, can be applied either to bulk or to wire manufacts [10,11] without the need of hot pressing apparatus. A selection of the typical bulk manufacts prepared in our lab is reported in Figure 10.

Fig. 10. MgB_2 bulk manufacts obtained by the RLI technology.

The peculiar microscopic morphology of the resulting material, illustrated in Figure 11, is characterized by large grains embedded in a matrix constituted by finer grains. This granularity does not prevent the flowing of the supercurrents through the grain boundaries, as was revealed by Magneto-Optical imaging [12].

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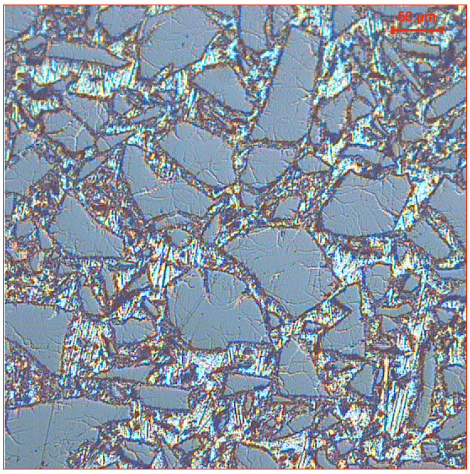

Fig. 11. Optical microscope image of a polished section of a typical bulk MgB_2 obtained by RLI

The superconducting characteristic of the RLI manufacts are similar to the best reported up to now, for samples obtained with more sophisticated preparative technologies [13,14]. As far as bulk samples are concerned the critical current densities at different temperatures and applied magnetic fields, measured in magnetization cycles, are displayed in Figure 12. The effect of doping, mainly C or SiC, in the increase of the flux pinning has been recently verified by several authors [15,16]. Experiments are underway if the same effects can be detected in the framework of the RLI techniques. Other outstanding characteristics of the bulk MgB_2 obtained by RLI are connected to the high values of the n exponent of the power law $V(I) \sim I^n$. The following simple exponential relation interprets the experimental values deriving from transport measurements of the V(I) [17] :

$$n(B,T)= n_o \exp(-\alpha B/(1-T/T_c)^{\beta}) \tag{1}$$

where n_o, α, β are scaling parameters. The scaling parameters found from a fit based on T_c=39 K are reported in Table 1.

Table 1. Best fit parameters for the n (B,T) formula (1)

MgB_2 Samples	n_o	α(1/T)	β
Bulk	103	0.30	1.33
Monofilament wire	130	0.38	1.00
7-filaments wire	37	0.145	1.33

As a practical benefit of the high n values of the bulk we have checked the possibility of having a persistent current in MgB_2 rings. In particular it has been verified that in rings of dimensions (ϕext/int=47/25mm; h=1 mm), immersed in liq. He, a remnant magnetic field of 0.51 T remains for more than 20 hours, after switching off an external field of about 1.5 T. The effective persistent current on the ring correspond to a density current of 1.250 A/mm^2 [18].

The present quality of the superconductive characteristics of the RLI bulk MgB_2 open the ways to applications at intermediate temperatures between 10 and 30 K and at intermediate magnetic fields , up to 2-3 T. The most appealing system should be the current leads, the permanent magnets for motors and shielding apparatus and also as variable inductor for Fault Current Limiters.

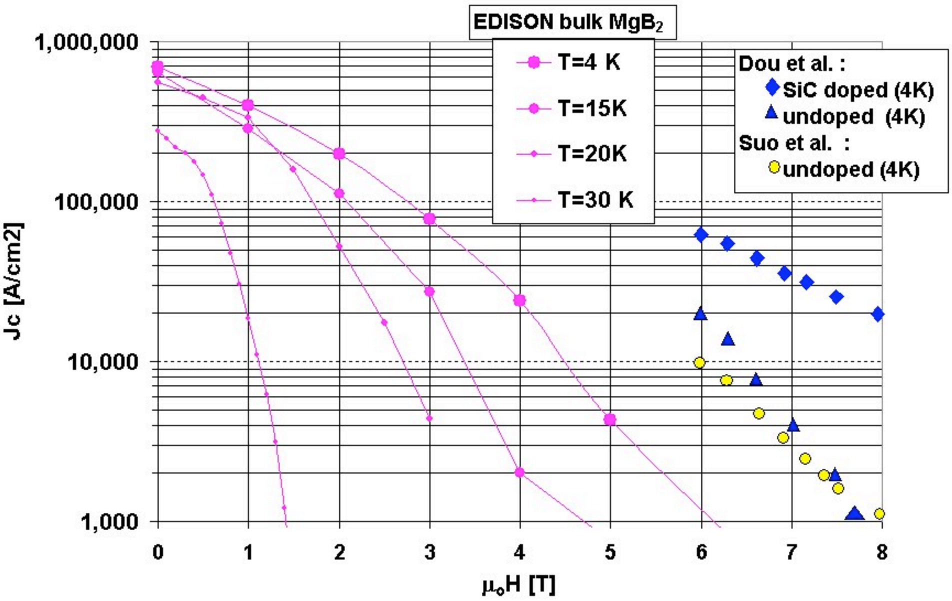

Fig. 12. Critical current densities of a bulk MgB_2 obtained by RLI, as compared with some outstanding samples (Dou et al. [13], Suo et al.[14])

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