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DEVELOPMENT OF HIGH CURRENT CARRYING CONDUCTORS FOR CABLES USING HIGH TEMPERATURE SUPERCONDUCTORS

Abstract

Five leading European electrical companies have been collaborating within the framework of a **BRITE/EURAM** project with the aim of selecting and developing a production technology for the construction of underground power cables containing high temperature superconductors. The **laser-melting** technique has been used to form conductors based on the Y-123 phase, and the powder-in-tube and various thick-film techniques have been applied to the bismuth-based superconductors. Thallium-based superconductors and selected 1212-phase cuprates were also examined for their suitability as HTS conductors. The most promising results were obtained with **(Bi,Pb)-2223** multi-filamentary powder-in-tube tapes, and two DC cable models have been designed, built and tested using these tapes. The best of the prototypes carried 430 A at 77 K in self-field.

1. INTRODUCTION

The long term objective addressed by this two-year **BRITE/EURAM** project is the development of high temperature superconducting (HTS) wire for use in underground power cables cooled by liquid nitrogen. These cables should offer reduced power losses and provide higher power ratings at lower voltage levels when compared with conventional copper cables of the same diameter. This would allow higher capacity superconducting cables to be retrofitted into existing underground ducts. Environmental benefits would also arise from the elimination of stray electromagnetic fields and the replacement of mineral oil as an insulating coolant by liquid nitrogen.

Considerable progress has been reported in the development of HTS wires during the last four years with the majority of these results obtained on powder-in-tube (PIT) processed tapes containing the **(Bi,Pb)-2223** phase (**BSCCO**) [1]. Recent notable results on short pressed tapes include a self-field critical current density (J_c) at 77K of 76 kA/cm² on a selected area of a sample [2] and a J_c of 69 kA/cm² measured over 2 cm [3]. Although these samples were fabricated using a pressing method which is not amenable to long-length manufacturing, the results demonstrate the considerable potential of **(Bi,Pb)-2223** conductors for high-current applications. Encouraging results have also been obtained on much longer rolled tapes, with J_c values reaching 17 kA/cm² over 100 meters with a good batch-to-batch reproducibility [4]. Also noteworthy are the recent improvements in critical current density obtained for highly-textured, polycrystalline YBCO thin films on metallic substrates; a self-field J_c of 1,300 kA/cm² at 75 K has been measured over 4 cm [5].

A key objective of this project was the design and fabrication of demonstrator conductors which were capable of carrying a DC supercurrent (I_c) of at least 100 A at 77 K in self-field. At the outset, it was unclear whether PIT processing of the **(Bi,Pb)-2223** phase would be the best method of producing the long lengths of HTS tape needed for these conductors, and so alternative materials and processing techniques were investigated in parallel. A laser-melting process was used to form yttrium-based conductors and various

thick-film techniques were applied to the bismuth-based materials. The fabrication of tapes containing thallium-based materials was explored and numerous lead-based, bismuth-based and other 1212-type phases were systematically synthesised using a laboratory robot and tested for superconductivity.

2. TECHNICAL DESCRIPTION

2.1. YBCO conductors

Two techniques were employed for the investigation of YBCO conductors. The first technique was a two-step operation involving the plasma spraying of a thick film of the Y-123 phase (YBCO) onto a metallic substrate followed by laser melting the film surface to remove the voids between the YBCO grains. The laser melting was performed using a CO₂ laser with a mean beam power in the range 400 to 500 W at 500 Hz (pulse time 1 ins). The scan rates were in the range 10 to 20 cm/min (giving an interaction time of 1 to 2 seconds) and post-annealing of the coatings was carried out at 880 °C for 2 hours in flowing oxygen. The best results were obtained using YBCO powder to which 10% silver had been added. This allowed the formation of a silver film between the metallic substrate and the superconductor which reduced the chemical interaction with the substrate and improved the adherence of the film.

For short samples, the best recorded critical current was 11 A corresponding to a J_c of 1,5 kA/cm² if the entire cross section of the film was taken into account. Analysis of the films revealed textured surface layers with low critical current densities, since a significant amount of copper was removed during the laser processing in the form of volatile compounds. In addition, a strong drop in critical current was recorded in an external magnetic field oriented either parallel or perpendicular to the scan axis confirming that the grains of the superconducting material in the centre of the films which carried the majority of the current were untextured and weak-linked, similar to the arrangement found in sintered bulk materials. The J_c of this portion of the film was determined to be 5 kA/cm², and it is assumed this relatively high current density for untextured material is due to the very clean grain boundaries produced by this process.

The laser melting process consistently led to loss of copper from the surface and produced inhomogenous coatings of poor strength and irreproducible superconducting properties. In order to overcome these problems, a new one-step technique was devised whereby the YBCO powder with 10% added silver is injected into the laser beam which is focussed onto the metallic substrate. The preliminary experiments on stainless steel substrates proved that dense superconducting coatings could be obtained using this laser-cladding process provided that the many process parameters were carefully controlled. A critical current of 25 A was obtained corresponding to a J_c of 1 kA/cm² for the entire cross section of the 500 μm thick coating.

The high thermal conductivity and lower melting point of silver or silver-alloy substrates required some modifications to the deposition parameters and substrate configuration in order to generate adherent coatings without melting the substrate. A thin YBCO-based black absorbing layer was sprayed onto the substrate in order to increase the absorption of

the 10.6 μm radiation emitted by the laser, and thermal insulating supports allowed the required deposition temperatures to be quickly reached without using excessive laser beam power. The optimal surface temperature range proved to be 1000 C -1200 °C, which led to the deposition of homogeneous coatings typically 100 μm thick without degrading the silver or silver-alloy substrates or decomposing the Y-123 phase. Below 1000 °C the adhesion was poor, and above 1200 °C the partial decomposition of the Y-123 phase resulted in porosity and cracking. By carefully controlling the thermal balance during the deposition, 30 cm long homogeneous coatings could be produced at 15 cm/min on 1 mm thick silver-copper alloy substrates supported on asbestos-based thermal insulators. The maximum coating length was limited by the available movement range of the 3-axis table used to support the samples,

Using 0.5mm thick silver substrates, 10 cm long coatings produced at 30 cm/min supported critical currents in the range 9- 11 A after annealing at 880 °C corresponding to a peak J_c of 1.9 kA/cm². In order to produce a conductor capable of carrying 100 A, similar coatings were then deposited onto 130 mm long, 17 mm ID and 19 mm OD silver tubes. The 1 mm thick tubes were coated with an YBCO-based absorbing layer and supported internally by thermal insulating rods made of porous alumina in order to prevent both excessive thermal transfer and deformation of the silver tubes. Good contact between the rods and the inside of the silver tubes was obtained by sheathing the rods with asbestos, Eight YBCO stripes were then deposited along the length of the tubes as shown in Figure 1 using beam powers in the range 650 W to 800 W at 10-20 cm/min, allowing the silver tubes to cool for a few minutes between each scan. A higher beam power was needed for the tubes compared to the tapes because of the larger volume of silver. After annealing at 880 °C, the critical current of each stripe was measured to be in the range 8 -11.5 A, confirming that it is possible to make a 100 A conductor using the laser cladding process,

2.2. *Thallium conductors and alternative 1212 phase materials*

A novel melt process has been reported to produce superconducting coatings of the thallium-based materials on ceramic substrate bars [6]. These coatings carry more than 100 A per cm width at 77K, and an attempt was made to reproduce this superconducting performance in coatings on silver substrates in order to produce a 100 A conductor. The films were formed by applying an upper thallium-containing layer to a lower BaCa₂Cu₂O₅ layer so that, upon firing, the upper layer melted and diffused into the lower layer to produce the superconducting coating. The BaCa₂Cu₂O₅ precursor coatings were formed on the silver substrates by powder spraying or using the laser cladding method developed for the Y-123 coatings. Powder slurries containing Tl₂O₃, Ba₃Cu₅O₈ and BaF₂ in various proportions were applied to the 50-100 μm thick coatings and the samples fired in air using a tube furnace with a thallium trap in a fume hood. Firing temperatures between 775 and 875 °C for periods of 1 to 8 hours were used.

Superconducting coatings were only formed if the samples were enclosed in silver foil to hinder the evaporation of the thallium. The homogeneous, but highly porous coatings were primarily composed of the Tl-2223 phase with a T_c of 118K, and typically carried 3 A per cm width of conductor at 77K. Experiments showed that mechanical pressing between heat treatments was very effective at densifying the coatings, and that the proportion of

the T1-1223 phase which has superior superconducting properties could be increased by altering the coating composition and the heat treatment parameters. However, the optimum set of conditions for this process had not been determined by the end of the project.

In parallel to the activity on the thallium-based materials, a robotic synthesis system was used to produce precursor powders for a wide range of cuprate materials [7]. The aim was to produce new superconducting materials amenable to melt-texturing using the laser cladding process or other thick film techniques. The robot produced complex oxides containing up to nine metals by mixing, drying and decomposing metal-containing solutions using ethylenediamine tetraacetic acid (EDTA) as a chelating agent. The oxides were then reacted in a furnace and tested for superconductivity using a SQUID magnetometer. A large number of 1212 phase materials containing lead, bismuth or transition metal ions in the non-superconducting ‘dopant’ layers were systematically synthesised and their properties studied. Many of these materials were new, some were superconducting but none of them have yet demonstrated superconducting properties at 77K which are suitable for use in conductors.

These experiments pointed towards the importance of high oxygen pressure synthesis as a means of increasing the calcium volatility of the phases and thereby improving their superconducting properties. The synthesis of bulk samples of (Pb,In)-1212 and (Bi,In)-1212 phases at 9S) °C in moderate pressures (~20 MPa) of oxygen was therefore attempted. However, this level of pressure did not produce any enhancement of calcium volatility but merely promoted the formation of impurity phases, and it was concluded that much higher pressures of oxygen are needed to produce 1212 phases containing only calcium ions between the CuO₂ layers in lead-based and bismuth-based materials. This hypothesis was subsequently conformed by the recent reports of Pb-1212 and Pb-1223 materials with T_c values up to 115K prepared using very high pressures (-5 GPa) of oxygen [8].

2.3. *Bismuth conductors*

Two coating methods were employed to produce thick films of the (Bi,Pb)-2223 superconductor: screen printing and doctor-blade coating. These methods, which use a mixture of precursor powder and organic binder, have a potential advantage over the powder-in-tube technique since the ceramic layer is directly produced on the substrate in a suitable thickness for a conductor, thereby minimizing the necessary number of thermomechanical processing steps. Moreover, multi-layer conductors can be readily produced by sandwiching these tapes together with additional silver or silver alloy foils in order to provide the essential mechanical and environmental stability. However, there are also potential disadvantages arising from the need to completely burn-out the organic binder to remove all carbon and the need to seal the edges of the tapes to prevent the loss of the melt during the reaction to form the (Bi,Pb)-2223 phase.

Broadly similar results were obtained using the two methods although the screen printing technique tended to produce slightly higher J_c values. Most of the research on the influence of the organic formulation and the residual carbon content on the reaction kinetics of the (Bi,Pb)-2223 phase was performed on printed tapes, and Figure 2 shows

the basic process for their fabrication [9]. The organic paste containing the precursor powder was first printed onto a silver foil. The best results were obtained using very fine grained precursor powder ($d_{50} = 1-2 \mu\text{m}$) made by a spray pyrolysis procedure which produced ceramic layers with a very uniform cross-section. The organic binder was then burnt out at temperatures around 400°C , and the sample uniaxially cold pressed at 10 kbar in order to densify the resulting porous ceramic coating.

In order to reduce the evaporation of lead during the subsequent heat treatments at higher temperature, a second silver foil was pressed on top of the ceramic coating. Trapped air within the samples causing blistering could be removed by sealing the samples under vacuum. The samples were then repeatedly fired at temperatures between 830°C and 850°C for periods of 70 to 100 hours with intermediate pressings at room temperature. The final thickness of the BSCCO layer was approximately $10-20 \mu\text{m}$. In the short samples made by this screen printing technique, the J_c values were typically $5 \text{ kA}/\text{cm}^2$, with the best J_c values extending up to $10 \text{ kA}/\text{cm}^2$.

Multi-layer samples were prepared by stacking and pressing together up to 7 single-layer samples topped by an additional silver foil, and the J_c values were generally similar to those observed on the single-layer tapes. However, a considerable improvement in J_c was obtained when two of the single-layer tapes were stacked and pressed with the ceramic coatings facing each other, thereby improving the uniformity of the silver-ceramic interface. J_c values of up to $16.5 \text{ kA}/\text{cm}^2$ were recorded on these samples which are the state-of-the-art for this technique. Unfortunately, there are practical problems to be solved before the technique can be scaled up to produce the much longer lengths of tape required for the assembly of cables. Furthermore, since the tapes require both pressing to achieve satisfactory densification and encapsulation to prevent phase degradation, it was concluded that the technique offers no immediate advantages over the PIT method.

In parallel with this work on thick films of (Bi,Pb)-2223 superconductors, effort was devoted to the preparation of long lengths of mono-core, multi-filament and stacked tapes using the PIT method. Each of the companies investigating this technique produced tapes using their own recipes, and considerable effort within the project was devoted to an exchange of samples and procedures in order to determine the key parameters required for good superconducting performance. Particular attention was paid to the specification and characterisation of precursor powder, both produced in-house and also purchased from commercial suppliers. The following process description refers to the methods used to fabricate the long multi-filamentary tapes required for the construction of the 100 A conductors.

Precursor powders were either produced in-house or purchased commercially with a nominal stoichiometry of $\text{BiPbSrCaCu} = 1.80:0.33:1.87:2.00:3.00$ (Endo composition [10]). The purchased powder had been produced by spray pyrolysis of the appropriate metal nitrates and calcined by the supplier at typically 800°C for 8 hours in a 21% O_2 -79% N_2 atmosphere. The specification for the powder determined that it should contain no more than 10% volume fraction of the (Bi,Pb)-2223 phase as determined from the X-ray powder diffraction pattern. Both 7-filament and 19-filament silver-clad tapes were then fabricated according to two distinct procedures.

For the 7-core tapes, the as-received powder was packed into a silver tube (10 mm o.d., 8 mm id.) which was then drawn to a diameter appropriate for the multi-filament assembly. 7 filaments were bundled together and packed into a silver tube of the same size as above. The multi-filamentary billet was then drawn and rolled to a final cross-section of approximately 3 mm wide by 0.2 mm thick. Two subsequent heat treatments were done in air between 830 °C and 845 °C for 50 hours with an intermediate rolling.

For the 19-core tapes, a one-stage loading method was used. Holes drilled in a silver billet 60 mm long and 49 mm in diameter were filled with solid rods of the precursor powder which had been prepared by cold isostatic pressing. The billet was extruded to 21 mm in diameter, and then rolled and drawn to a final cross-section of approximately 3.5 mm wide by 0.25 mm thick. Three subsequent heat treatments were done in air between 830 °C and 845 °C for 100 hours with intermediate rollings.

All critical current measurements were carried out in DC mode at 77 K and zero applied field using the four-probe method, with the contacts soldered onto the samples. The voltage criterion for the determination of the critical current was 1 $\mu\text{m}/\text{cm}$ and the cross-sectional areas of the tapes were determined by image analysis on at least two sections for each sample. The error on the area and hence the J_c value is typically $\pm 20\%$. The PIT processing route provided two types of samples, depending on whether pressing or rolling was used between heat treatments. Typical J_c values for short pressed samples were approximately 20 kA/cm^2 , whereas the J_c values of the longer rolled tapes produced as described above were approximately 10 kA/cm^2 .

The first PIT test conductor shown in Figure 3 was fabricated with a length of 1.3 m. A purpose-built computer-controlled cabling machine enabled the construction of the multi-strand conductor using 33 tapes helically wound onto a flexible former with a diameter of 40 mm using a pitch length of 330 mm. The I_c values of all the individual tapes were measured prior to cabling and summed to 114 A whereas the overall I_c of the cable model was 110 A. The construction of this model demonstrated that multi-filamentary PIT tapes are sufficiently robust to enable them to be wound into composite flexible conductors without adverse effect on their superconducting properties. Moreover, the critical current can be increased in an essentially additive fashion by winding multiple tapes into multi-strand conductors.

The second PIT test conductor with a length of 0.5 m was made by laying 10 straight bundles each of 10 7-core tapes into grooves cut into a flexible former with a diameter of 26 mm. The former also included a short section of copper rod, incorporating a current lead connection, attached at each end. More detailed measurements were carried out to characterise this second conductor [11]. The I_c values measured on individual tapes ranged from 5 to 11.2 A, with an average of 6.7 A. The I_c of each bundle was measured separately prior to mounting the bundle in the former and, in each case, the I_c was between 70 to 75% of the sum of the I_c values for the 10 tapes. In the case of the final conductor, pairs of voltage taps were soldered in three different configurations: in loops across the entire conductor, as contact points across one bundle of 10 tapes, and finally, across one tape. The I_c for the entire conductor was found to be 430 A measured over 40 cm, which corresponds to approximately 66% of the sum of the I_c values for the 100 individual tapes. Figure 4 shows the E-I characteristics for the entire conductor, the best

bundle and the best tape. The drop of I_c observed when successively testing the tape, bundle and conductor can partly be ascribed to mechanical damage incurred during the handling and soldering, and partly to the distribution of critical currents between the 100 tapes.

3. CONCLUSIONS

The partners have explored a number of materials and fabrication techniques with a view to determining the combination best suited for the construction of high temperature superconducting power cables. The fabrication of conductors containing the Y-123 phase or thallium-based materials was explored with promising results, but these conductors had not attained the required performance level over the long lengths needed for the construction of the demonstrator conductors by the end of the project. Numerous lead-based, bismuth-based and other 1212-type phases were also systematically synthesised and tested, but none of these materials exhibited superconducting properties suitable for HTS tapes when prepared under ambient conditions or under 20 kPa pressures of oxygen.

Both within this project and elsewhere in the world, the PIT processing of the (Bi,Pb)-2223 phase has emerged as a cheap and reliable manufacturing method for producing HTS tape with critical current densities suitable for use in cables. The present study first examined the technical issues and performance of short samples. Criteria were established for the selection and preparation of precursors, and good reproducibility of tapes was been demonstrated for J_c values in the range 10-20 kA/cm². Due to the relative ease of scaling up the powder-in-tube technique, long lengths of multi-filamentary tapes were fabricated and processed allowing two cable models to be designed and built with critical currents at 77 K and self-field of 110 A and 430 A. The partners have therefore established the essential capabilities to enable the next stage of development, the building of test sections of HTS power cable, to commence.

Acknowledgements

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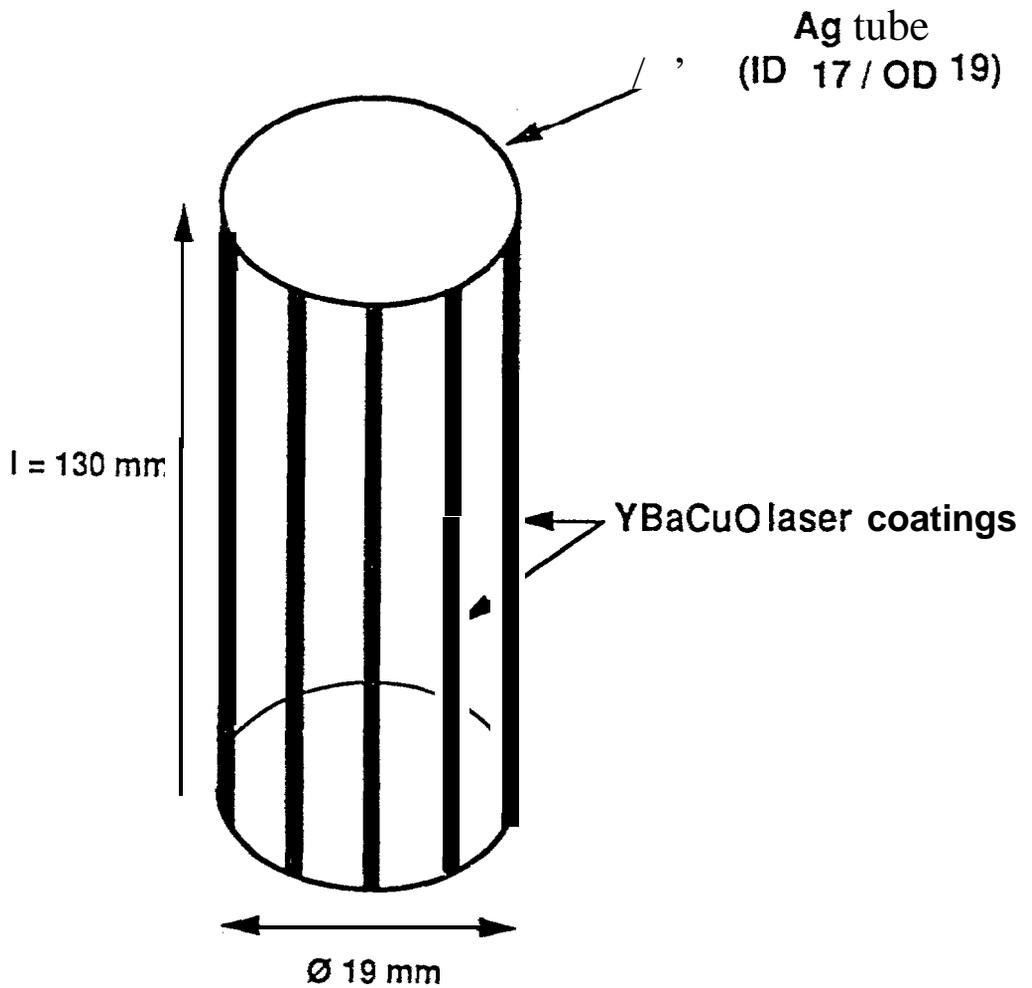
Figures

Figure 1: YBCO coatings on a silver tube.

Figure 2: Basic process for fabricating superconducting thick films of BSCCO on silver tape by the screen printing technique.

Figure 3: Photograph of the first multi-strand cable model containing 33 individual tapes.

Figure 4: E-I characteristics of the second multi-strand cable model containing 100 individual tapes: o best single tape; × best bundle of 10 tapes; □ complete conductor.



Results : I_c of single YBCO coatings = 8 - 11.5A

Figure 1: YBCO coatings on a silver tube,

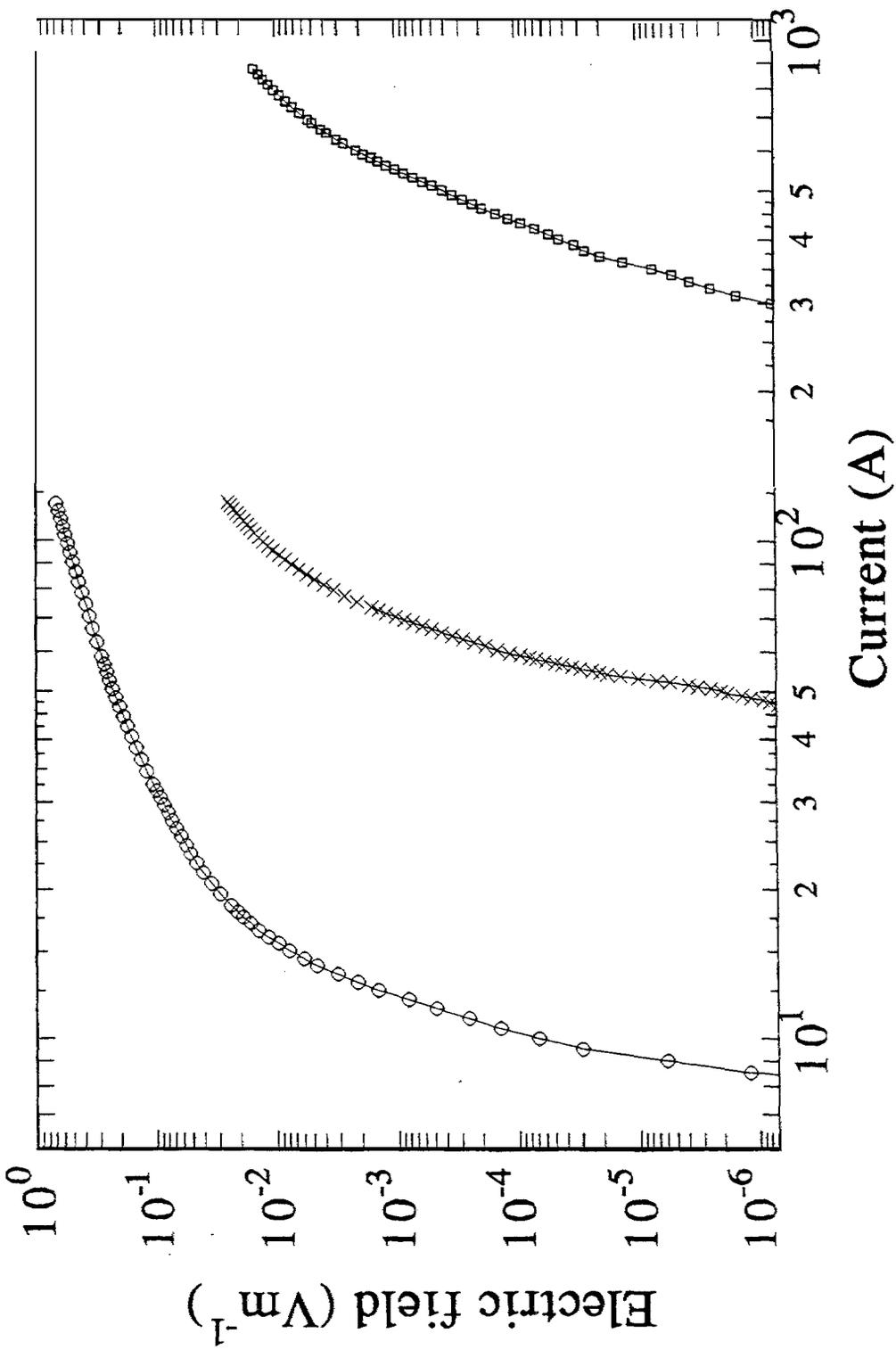


Figure 4: E-I characteristics of the second multi-strand cable model containing 100

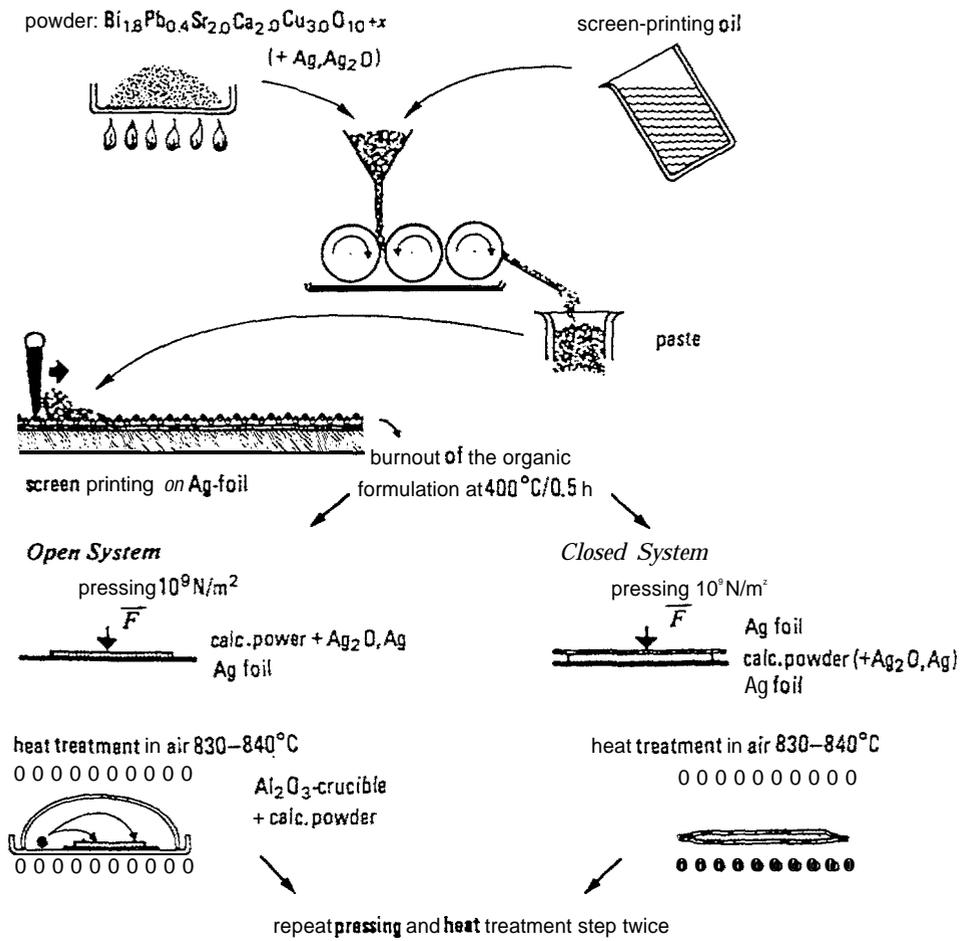


Figure 2: Basic process for fabricating superconducting thick films of BSCCO on silver tape by the screen printing technique.

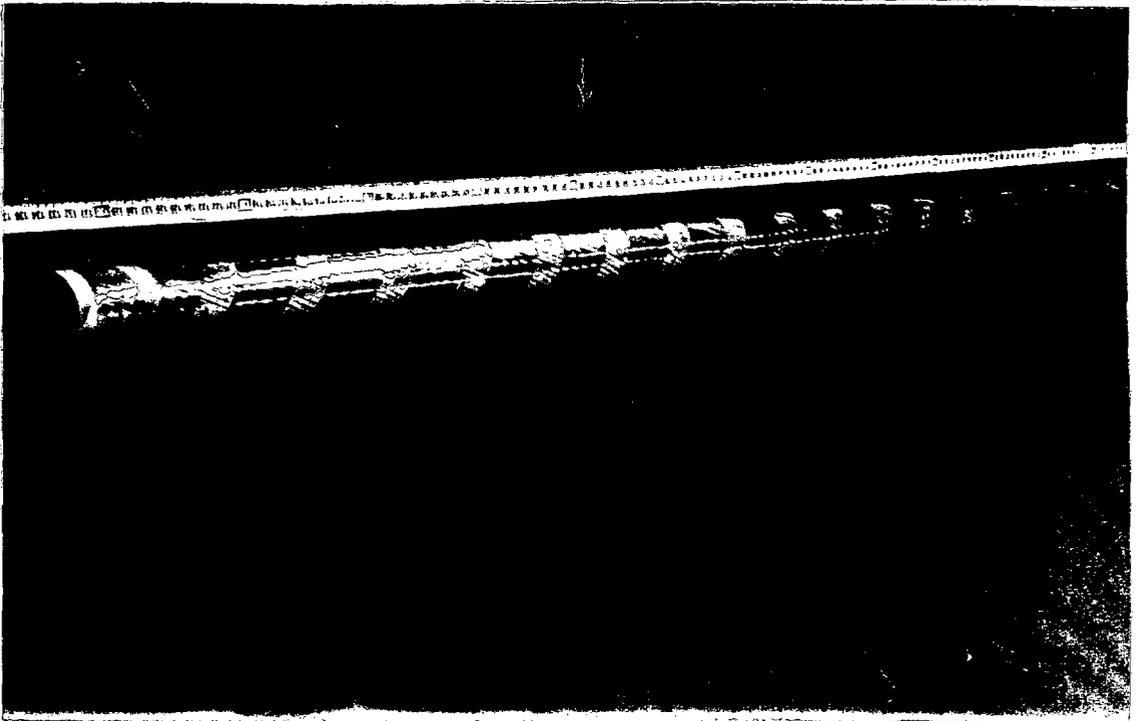


Figure 3: Photograph of the first multi-strand cable model containing 33 individual tapes.