Brite EuRam II
Project Number PLBE5399
Contract Number BRE2 -0208

Composite Reaction Texturing: A novel fabrication 'process for high Tc high current superconductor wires and shaped components

CREATE **Final Synthesis Report**

36 Month Project

Partners: University of Cambridge
NCSR Demokritos
Technical University of Denmark **(DTH)**

FINAL SYNTHESIS REPORT

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Project Number PLBE5399
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Composite Reaction Texturing (CRT) of High Temperature Superconducting Ceramics

Keywords: superconductor, composite, texture, seeds, cryogenics

Introduction

The , prospect for high-current applications of high temperature superconductors depends largely on innovation and the development of skills in materials processing. Several different approaches to fabrication have demonstrated the production of short lengths of conductor however few methods at present offer a realistic and economical route to the production of mechanically robust · high-current conductor with an adequate engineering specification. The main problems relate to the difficulty of scale-up to longer lengths and larger cross sections, and to the difficulty of handling fabricated conductors.

The primary technological objective of this proposal has been to develop, by focussed fundamental research, a novel process for the production of highly textured high critical current conductor. The method, termed Composite Reaction Texturing "(CRT), is a texturing process performed seeding the superconducting phase with a dense aligned distribution of unreactive second phase particles of suitable geometry, arid reacting the composite preform to nucleate and grow the superconducting phase with a texture determined by this second phase[2,3,5,7-20]. The main aim of this research has been to demonstrate that the CRT process can form the basis of a fully applicable materials technology. In the course of the project the detailed process steps have been assessed and optimised for the $Bi_2Sr_2CaCu_2O_x$ compound (Bi-2212) and a range of prototype artefacts have been demonstrated so that a realistic assessment can be made of the industrial promise of the new technology[11,15,17,18]. A secondary aim has been to demonstrate that the CRT process also has promise for the rare earth containing R-123 type compounds (eg. $YBa_2Cu_3O_7$). It has been shown that large artefacts with low angle grain boundaries can be fabricated using CRT techniques. Overall the CRT process has a number of unique features that distinguish it from other fabrication methods being investigated world-wide and make it attractive for industrial application. Conductors can be fabricated with a large cross-section to carry high currents and are. suitable for wind-and-react processing, the process does riot depend on a single solidification front and does not demand precisely controlled temperature gradients. CRT is a near-net-shape forming process; artefacts retain their shape during melt processing and the material can be machined to give detail and final engineering tolerances. Joints and robust high current contacts can easily be made[10,19]

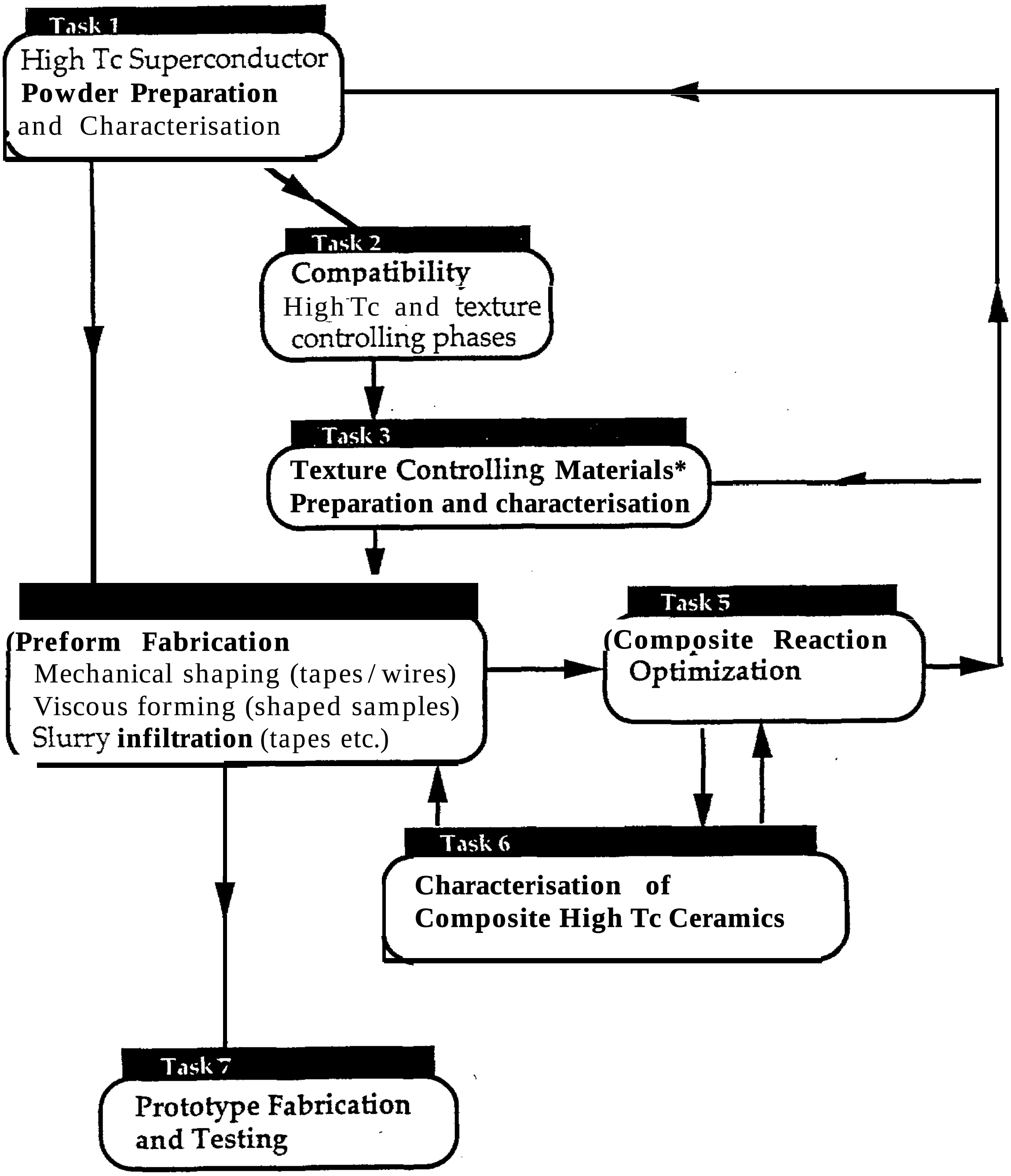
The partners (whose details can be found at the end of the report) brought complementary expertise to the project, Cambridge has experience in conductor design and the definition of an engineering specification for superconducting products, this is combined with advanced processing skills and broad experience in characterisation of microstrucures and measurement of superconducting properties. IMI, Copenhagen has deep experience of minerals and ceramic materials. Demokritos, Athens brought the special skills of sol-gel processing of particular interest for the production of complex superconducting compounds. The partners were supported throughout the project by five Industrial Sponsors who maintained an interest 'in the research and gave advice on commercial and applications issues. In particular Oxford Instruments gave advice on prototype product development and evaluated test material supplied.

Main Results

The principal tasks were related closely to the sequential stages of the CRT process (Fig. 1). In the first stage the components of the precursor composite were prepared and assessed. This involved the development of methods for the production of high quality inert seed material and, also, the production of suitable superconductor precursor powders. Also at this stage the compatibility of the materials was assessed and the nucleation and growth characteristics of different seed/superconducting compound combinations investigated. The basic requirement is the physical and chemical compatibility which allows (a) seeds to induce nucleation and texture the superconducting phase (b) seeds to remain inert during the reaction process so that the superconducting phase is not degraded. Thi work comprises the first three tasks, highlights were, (1) a very detailed scientific. investigation of the nucleation and growth of the MgO single crystal fibres used for CRT processed Bi-2212 material, and (2) a detailed study of the nucleation of R-123 compounds and the screening of a wide range of refractory compounds to assess compatibility and seeding characteristics. After proving that MgO fibers are suitable for texturing Bi-2212, we concentrated on the improvement of MgO-fiber-production processes. This was justified because, later in the project, we needed large batches of MgO fibers for the production of large prototype artifacts.

We tested a high number of potential seed materials for texturing Y-123 compound. After a comprehensive study, we demonstrated that R-123 single crystal seeds with melting points higher that that of Y-123 can be used as multiple nucleating sites in a CRT process, and developed various

Project Flow Diagram **Figure 1**



* Film-es, Whiskers and Platelets

techniques for the production of single crystal seeds of Nd-123, Sm-123 and Eu-123[14]. Although these seeds are compatible with Y-123 or Er- 123 compounds, a very close control of composite reaction parameters is necessary to prevent their dissolution during melt texturing. The seed production techiques make use of self-flux growth process and also requires a careful control of reaction parameters for reproducibility. Another important criteria in determining suitable seed material is the ability of producing it in bulk quantities. Due to the importance of this part of the project, we believe that there is a significant amount of benefit in screening many other candidates for better compatibility than that of high melting R-123 compounds. The basic work of the first stage of the project underpinned the whole project and resulted in three PhD theses and several published papers[2-6,14].

In the second stage (Task 4) methods" of fabrication of precision precursor composites with aligned seed material in superconducting compounds were developed and optimised with particular' attention to the requirement for future, scale-up potential. Various ceramic forming techniques were adapted to CRT to produce large size composite preforms[3,5,9-11,14,18,19]. In particular polymer processing techniques which make use of plasticisers, binders and solvents loaded with superconducting powder and seeding materials proved very versatile for the production of formable preforms. The viscosity of the product depends on the amount of solvent used in these mixtures, and this determines the choice of mixing, alignment and forming processes employed (eg. calendering or extrusion for viscous mixtures, doctor blade processing for liquid mixtures). The choice of forming processes is a critical parameter in aligning seeds. We found that, depending on the type of forming process we can align MgO fibers unidirectionally or random-in-plane, each alignment producing a different type of Bi-2212 texture[2,3,5,9]. A major achievement of the project was to demonstrate the range and versatility of these techniques, and joining techniques also developed in the project, for the production of highly textured sheets, multi-layers, tapes, rods, tubes and coils (Fig. 2). This work enables the applications engineer to design with confidence complex products to a particular mechanical and electrical specification.

The third stage (Task 5) involved detailed investigation of composite reaction procedures for optimizing the product microstructure and superconducting properties. The reaction process involves binder burn-off and a partial melting stage. In the case of CRT Bi-2212 material the process was investigated in scientific detail first to obtain a detailed understanding of the underlying texturing mechanisms and subsequently the optimum process procedures were determined so that a reproducible production route could be closely specified. Remarkable observations were made of the nucleation and growth process and the dependence of the final texture

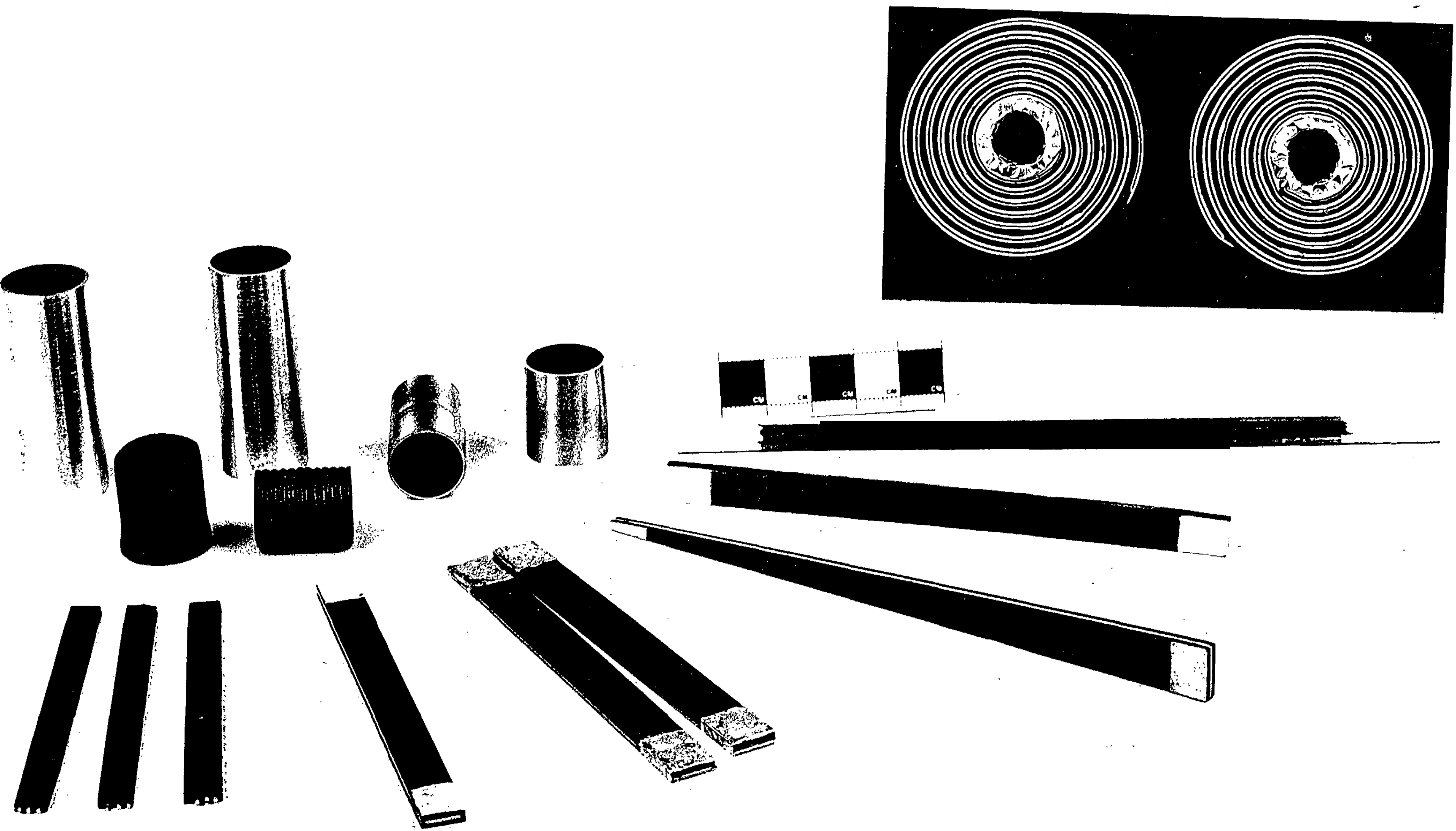


Fig. 2 CRT processed prototype artifacts; current leads, shielding enclosures (tubes) and pancake coil (inset)

type on the distribution of seed material Fig.(3) [2,3,8,16]. Our detailed High Resolution Electron Microscopy work on the low angle boundaries revealed that the boundaries exhibit changes in the local composition as well as in the s tructure[8,16]. A particular feature of the CRT process is that the shape of the artefact is retained through the melt processing stage. All stages of this work have been published or are in preparation for publication [1-19].

Although CRT R-123 material has greater potential in the long term for high field high current applications at 77K the processing problems are very much greater because full hi-axial texture is essential to avoid the weak-link problem. With the resources and time available it was decided only to demonstrate the main elements and promise of CRT processing for R-123 materials. We therefore developed techniques to hi-axially align the seeds magnetically and/or mechanically and demonstrated for the first time full hi-axial texture with multiple-growth from a spaced array of seeds[14]. Multilayering techniques were used to enhance and control growth and we obtained low angle and clean grain boundaries for neighboring Y- 123 crystals, each nucleating on a separate seed. The high quality of the samples produced brought very considerable problems of oxygenation and impeded full electrical characterisation of the samples.

The fourth stage of the project (Tasks 6 and 7) involved prototype fabrication, electrical, mechanical and environmental studies, to, (1) provide information for product design, (2) assure reproducibility, (3) enable process optimisation and, (4) facilitate quality control in prototype products. Extensive transport current and magnetisation measurements as a function of temperature, applied magnetic field and sample type and geometry have established that large cross-section CRT Bi-2212 samples can have a critical current density, J_c, in excess of $5x10^4 A cm^{-2}$ at 5K and 12 Tesla. At 77K J_c is in the range $4x10^3$-$10^3 Acm^{-2}$ depending on the self-field[2,3,10,11,17]. These values are comparable to those obtained by other workers for thick film Bi-2212 samples.

Currently only the Bi-2212 process has been developed to the point of engineering applications. The following applications were explored.

- **Current Leads**

Good progress was made on this, application, several designs are of interest for different cryogenic systems (conventional, cryogen free, ultra low loss etc.). For example twin tapered profile current leads with stainless steel reinforcement, low thermal conduction losses and reliable contacts were developed[11]. Oxford Instruments plc, Cryogenic Ltd, and Florida State University are collaborating in the evaluation of prototype current leads.

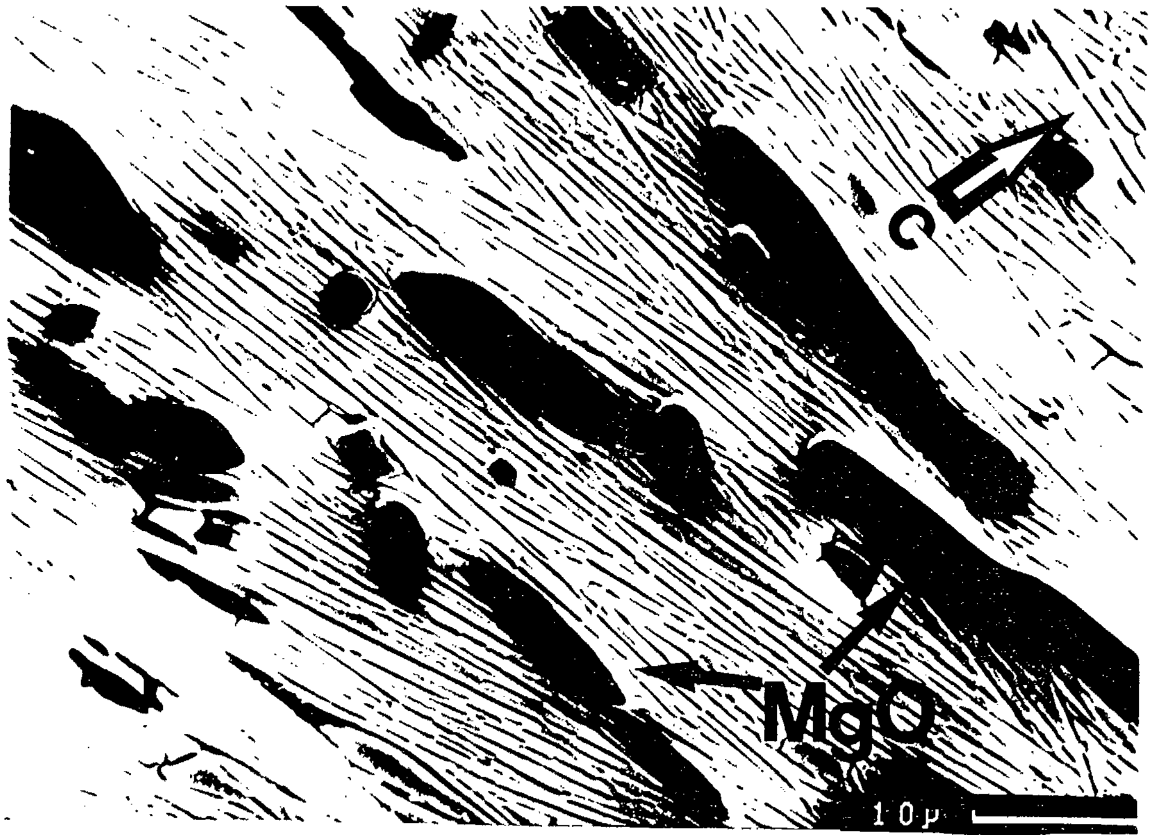


Fig 3 Cross-sectional SEM micrograph of a Bi-2212 sample showing the texture development

- **Fault Current Limiter Components**(12, 17)

The CRT process is able to fabricate monolithic and modular reinforced cylinders as well as linear transport elements suitable for various Fault Current Limiter (FCL) applications. The CRT Bi-2212 seems particularly suited to FCL applications because of its sensitivity to magnet fields at 77K and because the material is supported by the MgO reinforcing material during processing thereby retaining any chosen design configuration. One of the most important design criteria of these products was their mechanical strength which made us consider several options as reinforcement materials. We can produce cylinders and tubes with stainless steel or nickel reinforcement with a silver buffer layer to prevent contamination during the reaction process. The other alternative to join the reinforcement material after the production using epoxies. A number of major consortia are interested in the process. Measurements of the screening properties of reinforced cylinders for an inductive FCL have so far been made in collaboration with the Hydro Quebec/S iemens consortium. A new Rolls Royce/EA Technology FCL consortium is investigating the material and has employed one of the staff from the CREATE project. In addition Brown Boveri are interested in aspects of the CRT process for their FCL programme and have employed a second staff member from the project.

- **Screening Enclosures**(12, 17)

This application experienced good progress with the development of techniques for preparing monolithic and modular reinforced cylinders. Measurements of the screening properties of reinforced cylinders (albeit for fault current limiter applications) were made in collaboration with Hydro Quebec.

- **Other Applications**

Several other application areas are being closely assessed and test components are being fabricated in co laboration with different organisations. A superconducting synchronous motor is being developed with Oxford University; multilayer CRT processes are being developed for the production of monolithic pancake coils[15], for magnet inserts (Cryogenic Ltd, National Magnet Laboratory, Florida). Components depending on the strong characteristic anisotropy of CRT material are being assessed for application in switches and flux pumps.

Summary

In the course of this three year Brite-EuRam Project a new process for advanced conductor fabrication has been developed from initial conception to a **fully applicable technology** that is already taking an important place in a number of application areas. The Composite Reaction Texturing

(CRT) process developed has many features that are unique and it is very likely that it will take an important position amongst those processes that are eventually selected for full commercial production. The particular features of the CRT process are: the CRT process is European technology patented world- wide[20]; the process can be conveniently applied to large conductors of arbitrary shape and cross-section; CRT is suitable for a form-and-react or wind-and-react type of fabrication technology, joints and contacts can easily be made; the process is a near-net-shape forming process and therefore very economical on material; the reaction process is relatively rapid and does not depend on a single solidification front; large complex artefacts have strength during the melt reaction process and retain their their shape; the processing steps are not particularly demanding; it is possible to fabricate very high critical current conductors, because the conductor cross-section can be large.

As a result of this project, 19 publications and four theses were produced up to now. Our work has attracted attention at the American and European Applied Superconductivity conferences and a recent international report on “High temperature superconducting bulk high-ampere conductors” (prepared by Argonne National Labs-USA, for the International Energy Agency, October 1995) has included a section on Composite Reaction Texturing and mentioned it as one of the most significant techniques for the fabrication of bulk high temperature superconductors.

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