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NOTE:

It has not proved possible to write one coherent report in the style of a research paper covering all the work undertaken in this project. This is because the programme of work as originally conceived contained two parallel areas of investigation with very little overlap. In order to prepare appropriate technical presentations of the work, it has been decided to write two independent papers covering the complete range of work completed in the project.

Fabrication and testing of Tl-1223 superconducting coils

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Abstract

We have investigated each stage in the processes required to fabricate superconducting coils from Tl- 1223 superconducting material; including po waler synthesis and composition, mechanical processing, the relationship between microstructure and superconducting properties and strategies for achieving grain alignment, in order to optimise a process route. A novel melt process for Tl-1223 tapes has been studied in detail. We have also investigated the technical aspects of coil fabrication and measured the properties of some demonstrator coils over a wide range of magnetic fields. Engineering critical current values over 3,000 $Acr^{e-}2$ have been reproducibly achieved, and demonstrator coils more than 10m in length have been tested in high magnetic fields.

Introduction

The fabrication by the powder-in-tube technique of Tl- 1223 tape for use in applications such as magnetic field generating coils is being studied by several groups [1-3]. At present most work is directed towards the optimisation of tape properties, although coil fabrication aspects, such as how to provide inter-turn insulation and whether to follow wind-and-react or react-and-wind strategies, must also be investigated. There is a wide range of possible compositions for the 1223 phase. Typical substituted compositions are $(Tl_{0.5}Pb_{0.5})(Sr_{1.6}Ba_{0.4})Ca_2Cu_3O_x$ [1,3] -and $(Tl_{0.78}Bi_{0.22})(Sr_{1.6}Ba_{0.4})Ca_2Cu_3O_x$ [2,3], and the precise composition influences both the processability and the eventual superconducting properties of the finished tape. We have therefore investigated each stage in the coil fabrication process, including powder synthesis and composition, mechanical processing, the relationship between microstructure and superconducting properties and strategies for achieving grain alignment. We have also investigated the technical aspects of coil fabrication and measured the properties of some demonstrator coils over a wide range of magnetic fields. .

Sample characterization techniques

The phase purity of all our Tl-1223 powders was assessed by X-ray diffraction. The microstructure of silver alloy sheathing materials was studied by conventional optical microscopy, and hardness and tensile tests taken to assess mechanical properties. Polished cross-sections of the tapes were prepared using standard metallographic techniques to investigate core and grain morphologies. SEM and EDX analyses were carried, out on a scanning electron microscope fitted with an EDX system- Tc and Ic values were measured using the usual 4 point method using criteria of 0.1 μVcm^{-1} and 1 μVcm^{-1} respective y. Magnetisation measurements on inter and intragrain critical current values were carried out in a VSM and interpreted using a generalised Bean model. TEM analysis was carried out on cross sectional and plan view samples of some of the tapes.

Powder fabrication

Tl- **1223** powders were fabricated using a variety of compositions of $(Tl_{1-x}Bi_x)(Sr_{1-z}Ba_z)_2Ca_2Cu_3O_\delta$. **A** precursor powder was fabricated from $SrCO_3$, BaO., CaO and CUO by heating at 940°C for 16 hours, regrinding and repeating the procedure three times. Tl_2O_3 and

Bi_2O_3 were then added in stoichiometric amounts. Superconducting powder was made by reacting this mixture in a sealed alumina crucible at 940°C for 2 hours. A Ba- and Bi-rich impurity phase can be identified by EDX analysis and is usually attributed to a substituted $BaBiO_3$ phase [4], although we propose a different structure below. A reliable synthesis route for the $Tl_{0.5}Pb_{0.5}Sr_{1.6}Ba_{0.4}Ca_2Cu_3O$ compound has also been demonstrated from simple oxide mixtures at 905°C for 2.5 hours. The only significant impurity phase is $BaPbO_3$. "

Effect of composition

The role of Bi and Pb substituting for Tl (and Ba for Sr) in powder and tape samples has been investigated. Ba substitutions have been found to aid the formation of the 1223 phase, lower the reaction temperatures and widen the reaction windows. Bi substitutions have also been observed to increase the grain size of the powder, and Tc was found to rise to a maximum of 112K for $x=0.2-0.25$. It has subsequently been established that Bi has a substitution limit of 0.25 due to ordering of the Tl and Bi [5]. Pb substitution also improves the reliability of the synthesis process. Magnetisation data was obtained for powder samples substituted with Pb or Bi, or with no substitution, on the Tl site. The intra-grain Jc values were very high for all the Tl-1223 samples, and especially in the Bi substituted materials remained high even at temperatures well above 77K, Figure 1.

Microstructure and mechanical properties of sheath materials

Most of the work on HTS wires and tapes worldwide has concentrated on using pure silver as the sheathing and support material. We have investigated new sheath materials to achieve increased mechanical strength to support larger stresses during mechanical processing. Most of these alloys are not commercially available and were prepared specially for the project by Engelhard-CLAL. Ag-0. 1 % Hf, Ag-0. 1 % and 1.0% Mg alloys were prepared in the form of 12.5mm diameter rods and processed into 6mrn diameter tube bys waging and drilling to 4 or 4.5mm internal diameter. Two Ag-Mg-Ni alloys of the composition commonly used for electrical contact alloys have been studied: Advent Ag-0.28%Mg-0.20% Ni (in the form of 4mm x 3mm diameter tube) and Engelhard-CLAL Ag-0.25%Mg-0.25% Ni (in the form of 0.25rnm thick ribbon). The main emphasis of this work has been to identify the combination of mechanical properties in a sheathing material most suited for the thermal/mechanical processing undertaken on the Tl-1223 tapes described below.

The routine production of high quality wire from silver/alloy tubes requires an optimised interstate annealing process. Material was first examined in the cold worked condition and then after annealing at temperatures ranging from 150-550°C in air. The cold worked microstructure of each of the materials is typical of a heavily worked ductile metal. Microstructural changes start to occur even at 150°C. An initial transition to a strain-free microstructure, followed by a gradual increase in grain size with increasing annealing temperature was observed in pure silver and all the silver alloys with the exception of Ag-0. 1% Hf. In this alloy system, increasing the annealing temperature resulted in a reduction in the grain size - possibly due to the development of a fine sub-grain structure. Samples were also heat treated at 850°C for 0.5h. In each case the grain size is increased - even in an initially 'strain-free' material. Of all the alloy compositions, the Ag-Mg-Ni alloy retained the finest grain size at elevated temperature.

The hardness of the sheath materials was also monitored after low temperature annealing. For a conveniently short annealing time of 5-10 minutes, (a) pure silver can be annealed at 300-400°C, (b) Ag-0. 1 %Mg at 250-350°C and (c) Ag-0. 1 %Hf at 450-550°C. Similar tests were carried out at a typical reaction or sintering temperature of 850°C. Figure 2 shows that Mg, which is internally oxidised at high temperature, is a very potent hardening addition. Peak harnesses of 100 to 200Hv were observed for Ag-0. 1 %Mg and Ag-1.0%Mg respectively. The AgMgNi alloy hardness falls in the middle of this range. Even though the increase in hardness, particularly in AgMgNi, resulted in very good core compaction and stability, the silver loses a significant amount of its inherent ductility. The very rapid rise in hardness with process time would require impractically short heat treatments to avoid brittleness. The slightly slower hardening response of the Ag-0.1%Mg alloy was reflected in a slight improvement in ductility, compared to Ag MgNi, but still required extreme care in handling to avoid breakages. The Ag-0.1%Hf was the only alloy system that did not suffer from embrittlement after processing and also showed some increase in hardness compared to pure silver.

It is commonly suggested by workers on PIT processing that increased sheath strength can lead to improved core compaction through more effective load transfer, so a series of tests was carried out to determine the work hardening response of various silver/alloy sheathing materials in tape form. Both pure silver and Ag-0.1%Hf tapes show an initial rapid increase in hardness at 10% reduction, followed by a slower almost linear increase from 20-80% reduction. Little difference is seen in either case between samples that were annealed at 400 or 850°C. At the highest reduction (80%), Ag-0.1%Hf shows a small increase in hardness over pure silver. The hardening behaviour of the Ag-0.1%Mg and Ag-Mg-Ni alloys is very different. In both cases, high temperature processing results in widely separated hardness data for material heat treated at 400 or 850°C. In addition to hardness testing, tensile testing was also carried out on all the sheath materials and the results are summarised in Table 1.

These results show that for the sheath materials studied in this project, only Ag-Hf can offer an improvement in strength together with the good ductility required for multistage annealing and coiling operations. We have fabricated long Tl-1223 tapes with extremely uniform superconducting properties in the Ag-Hf alloy.

SHEATH MATERIAL	SAMPLE condition	TEST temperature	Hv ($kgmm^{-2}$)	Tensile Str. (MPa)
pure silver (99.99% purity)	rolled	RT	99	248
	"	77K	145	253
	annealed	RT	30	128
	"	77K	39	149
Ag-0.1%Hf	rolled	RT	96	
	swaged	RT	72	227
	annealed	RT	33	170
Ag-0.1%Mg	rolled	RT	88	
	annealed	RT	108	
Ag-1.0%Mg	rolled	RT	112	
	annealed	RT	188	
Ag-0.25%Mg-0.25%Ni	rolled	RT	123	457
	annealed	RT	174	409
Ag-0.28%Mg-0.20%Ni	rolled	RT	106	237
	"	77K	203	404
	annealed	RT	173	484
	"	77K	205	705

Table 1. A compilation of the mechanical property data obtained on the sheath alloys studied in this project.

Tape fabrication

Reacted superconducting powder was fabricated using a '$Sr_{1.6}Ba_{0.4}Ca_2Cu_3O_x$' precursor and Tl_2O_3 and Bi_2O_3 as previously described [6]. PIT tapes were fabricated from both reacted powder and an unreacted precursor mixture using conventional drawing and rolling process to a final thickness of 50-200μm.

Methods to pack tubes

Four methods of packing silver tubes were investigated: [a] tapping, [b] ramming, [c] pressing and [d] ram and press. The pressing operation is carried out with a force of 10kN leading to an applied pressure of approximately 0.8GPa. The highest core fraction at the end of the wire drawing process is produced by methods c and d, and these values are little changed from the initial cross-sectional superconductor core fraction of 0.44 for a typical 6 x 4mm diameter tube. Specimens prepared without ramming showed large scale porosity after a heat treatment of 30 minutes at 840°C. After further rolling and heat treatments at 840°C for 7.5 hours, the packing methods that involve pressing clearly give the larger core fractions for tape thicknesses down to about 0.1 mm. The highest engineering Jc values in this thickness range were found in tapes prepared by method d, and we have established that the advantage lies not in improved properties of the superconducting material, but in the increased core fraction.

The effect of final wire diameter

Tapes containing unreacted Tl(Bi)-1223 precursor powder were drawn to diameters between 0.75 and 2 mm. All were subjected to identical subsequent thermal/mechanical treatment, and when the critical current densities are calculated and plotted, Figure 3(a), a substantial increase with decreasing wire diameter is immediately, clear. Similarly, TI(Pb)-1223 wire drawn to diameters between 2.36 and 0.3mm was heat treated at 840°C for 10 hours. The resulting engineering Jc values are shown in Figure 3(b), with a significant increase in E-Jc values as the wire diameter is decreased. The highest E-Jc values of 3,000-3,500 A/cm^2 are found in the tapes rolled from the smallest diameter wires and correspond to Jc values in the core of 11,000 A/cm*, Longitudinal optical micrographs show that irregularities in the core (sausaging) are reduced substantially by rolling thinner wire.

Pressing

We investigated the effect of pressing on both Tl(Bi)- 1223 and Tl-(Pb)- 1223 wires drawn in AgMgNi tube from a starting diameter of 4.6mm down to approximate y 1 mm. Results for Pb-substituted samples are shown in Figure 4 which plots the E-Jc values as a function of the initial wire diameter for various pressing loads. The combination of small initial wire diameter and pressing at 10 tons is clearly effective at increasing the E-Jc values well above 3,000 A/cm^2. In pure silver sheaths we have observed increases in Jc values of about 25% after pressing,

Rolling reduction

The amount of reduction applied per pass in a rolling process 'can have two major effects on the deformation process of a metal-sheathed ceramic tape; the larger reductions result in higher rolling forces, and the geometry of the rolling process is altered. Tapes containing pre-reacted Tl(Bi)- 1223 powder (which only requires a single sintering heat treatment) were rolled to nominally the same final thickness in pure silver and alloy sheaths using rolling reductions from 2.5% (55 passes) to 80% (1 pass). Figure 5 shows that a higher rolling reduction can have a significant effect on the critical current values, although part of this improvement is due to the increasing width of the tapes.

Heat treatment processes

Process (1)

The first thermal process is the most straightforward since it uses fully reacted Tl- 1223. The thermal/mechanical processing that is required to form a conductor is therefore a standard ceramic sintering operation in which the two main process variables are compaction (determined by rolling/pressing load and deformation geometry) and sintering (determined by temperature and time). In addition to being a relatively straightforward operation, the processing window for the sintering of Tl(Pb)- 1223 and Tl(Bi)- 1223 superconductors is very broad, both in terms of temperature and time. In Tl(Pb)-tapes the Ic values are relatively insensitive to process conditions between **830** and 860°C for annealing times between 5 and 20 hours. The highest Ic values are found in tapes containing powder of stoichiometry $Tl_{0.575}Pb_{0.425}$ sintered at 840°C. In Tl(Bi)-tapes the sintering behaviour is similar, with the highest current densities being obtained across a rather wider {temperature range, 800 - 860°C.

Process (2)

In Process (2) the starting powder consists of an intimate mixture of $(SrBa)_2Ca_2Cu_3O$ precursor and Tl and Bi (or Pb) oxides. We have followed the thermal/mechanical process suggested by Ren and Wang [2] where the Tl- 1223 is at least partially formed in a short first heating stage and subsequent deformation and further heat treatment steps result in further consolidation and reaction of the superconductor. The 'introduction of intermediate deformation stages during tape processing complicates the thermal/mechanical processing as the stage I tape thickness is now also a variable. We have established that a stage I thickness of 0.3 to 0.4mm results in maximum current density in tape of final thickness .0. 15mm. A set of samples were rolled to the optimum stage I thickness of 0.35mm and annealed for 0.5h at temperatures ranging from 760-880°C before rolling to O. 15mm and annealing for 7.5h at temperatures ranging from 800-860°C. Figure 6 shows that for the given process times, a maximum critical current density in the core of around 8500 Acr^{e-}2 was achieved with stage I: 820-860°C and stage II: 820-840°C. To achieve optimum Jc values, a minimum stage I time of 10-20 min and a minimum stage H time of 6-7h is required. The stage I process time may be extended to 60min with no deterioration in Jc, whereas the stage 11 process time should not exceed 12h.

Process (3), Melt processing

Processes 1 and 2 produce Tl- 1223 tapes with very small grains and no grain alignment. In order to attempt to produce Tl-1223 tapes with much larger grain sizes, we have established the feasibility of a melt processing route for Tl- 1223 tapes and have investigated the effect of various processing parameters. Tape samples were fabricated from both reacted and unreacted powder of various compositions $(Tl_{1-x}Bi_x)(Sr_{1-z}Ba_z)_2Ca_2Cu_3O_\delta$. Tapes made with reacted powder were found to give more reproducible I_c values and a much larger grain size than tapes fabricated from unreacted or partly reacted powder. A melt temperature in the range 920-925°C was found to lead to decomposition of the 1223 phase forming 1212 and SrCaCu oxides. These phases react to re-form 1223 on further heat treatment. Further small particles of a Tl-Ca-AgO and a Ba- and Bi-rich phase were also identified by Electron Probe Microanalysis (EPMA), but these were not found/o re-form into the 1223 phase. Cooling rates from the melt of 10-240°C/h were studied, and slower cooling rates were found to result in larger grains after further annealing. Grains up to 60-70µm long for reacted powder and 20-30µm long for partly reacted powder can be routinely obtained. The 1223 phase begins to re-form in the cooling step . (slower rates are found to lead to increased 1223 formation in this step) and the annealing stage completes the reaction. However some 1212 and SrCaCu oxides (1!3-20% estimated by X-ray Diffraction (XRD) depending on the conditions) do remain and we have been unable to achieve greater than about 80% phase purity in tapes containing large grains. We believe that this is due to the formation of the stable Tl- and Bi-rich secondary phases which result in a non optimum composition in the remaining core material and therefore a greater fraction of 1212 and SrCaCu oxide particles. Tc values of 114- 11.5K and Ic values of 6-7A are routinely obtained, indicating that this process has much potential for further development.

These results suggest that a decrease in porosity and a thinner superconducting core would lead to an increase in grain alignment and improved properties. We have tried a number of methods including multiple stage melt and deformation processes and the fabrication of multifilamentary tape. Our most successful improvements were gained through the use of multi filamentary tape. Figure 7 indicates that in very thin cores grain alignment can be achieved, but this type of core restriction is not easily achieved in continuous fibres using a PIT process. Our results also show that the optimum processing window is a compromise between the melt temperature and the cooling rate and that these parameters must be carefully controlled to, achieve aligned grain growth.

Effect of Bi substitutions

The effect of Bi substitutions were studied by fabricating tapes from reacted and unreacted powders of $Tl(_{1-x}Bi_x)(Sr_{0.8}Ba_{0.2})_2Ca_2Cu_3O_x$ composition with Bi substitution levels of x=0, x=0.15, x=0.22 and x=0.3. Three types of tape synthesis conditions were investigated, an in-situ reaction or sintering heat treatment at 840°C and a melt processing route. A range of melt temperatures and cooling rates were studied as these parameters have been shown to have the most influence on microstructural development.

Melt Processing conditions Tapes fabricated using unreacted precursor of compositions x=0 and x=0.3 were heated at 840°C for 6h before melt processing at 920-925°C and cooled at 40°C/h to 840°C for 6h. XRD analysis of tapes of composition x=0 showed 1212 phase even after extended annealing. By contrast, tapes of composition x=0.3 showed the formation of 1223 majority phase for these conditions. Tc values are therefore much higher in these second samples, 114-115K with Ic values of 3-3.5A. Optical micrographs of the samples show a more platy microstructure and a larger grain size than achieved with x=0.15 or x=0.22 compositions. These results show that Bi substitutions are important in the formation of the 1223 phase in tape processing conditions. This is surprising given that $Tl(Sr_{0.8}Ba_{0.2})_2Ca_2Cu_3O_x$ can be easily synthesised and suggests that the reaction conditions in the tape are radically different to those in a conventional powder synthesis process.

We have carried out a more detailed studied of the effects of Bi substitutions for reacted precursors as the effect of the processing parameters in our melt process has been more closely defined for a reacted powder precursor. The effect on decomposition behaviour was investigated by quenching tapes from temperatures in the range 910-925°C. XRD analysis of the opened tapes showed some decomposition of the x=0 phase at 920°C and almost complete decomposition into 1212 phase at 925°C. Fully melt processed tapes were found to have the platy microstructure typical of the melt process. Tapes of "composition x"=0 were found to contain larger grains than the Bi substituted samples at all the melt temperatures. This is in direct contrast to the effects seen in the tapes made with unreacted precursor. These results suggest that once the 1223 phase is formed, Bi substitutions increase the stability of the 1223 phase and lead to an increase in the melt temperature. This therefore leads to a decrease in the grain size obtained for a given melt temperature. TEM analysis of these samples showed a well connected grain structure of Tl-1223 grains with no evidence or impurity phases at the grain boundaries, Figure 8.

Ba- and Bi-rich secondary phases Bi containing powder samples are found to have increasing secondary phase peaks for increasing Bi substitution [10]. These peaks are usually identified as $BaBiO_3$ although the peak match is not precise. It is usually assumed that there is a degree of cross site substitution and that the composition is $(Ba/Sr)(Bi/Tl)O_3$ which would slightly alter the lattice parameters. We have used TEM analysis to show that these Ba and Bi rich particles also contain the elements Sr and Ca, and have a layered structure with a c axis of about 12.5Å, Figure 9. In order to determine whether a phase of this composition could have peaks in an XRD pattern similar to those of $BaBiO_3$ we have carried out some synthesis experiments. We estimated that this phase could have an approximate composition of 2Ba:2Bi: 1 Ca. Synthesis experiments using this composition showed that a phase with peaks similar to those of $BaBiO_3$ could be fabricated, and we believe that this is the new phase with a layered rather than cubic structure and a composition of around $Ba_2Bi_2CaO_x$ with a small fraction of substituted Sr.

Superconducting properties

The Ic and Jc values of some of the tapes prepared in this work have been described above. Summarizing these results; Ic values as high as 20A, core Jc values above 11,000 Acm^{-2} and engineering Jc values of 3,500 Acm^{-2} have all been achieved reproducibly in Tl- 1223 tapes at 77K in zero applied magnetic field. We have also investigated *self field* effects in these tapes [6] and found them to be very severe as a result of weak links in the material. The weak link behaviour has been carefully analysed by Ic/B measurements of the kind shown in Figure 10, where the Ic values drop by a factor of 20-30 as the applied magnetic field is increased to 200G.

Coil fabrication

While there are two approaches to coil fabrication, react-and-wind or wind-and-react, we have concentrated on making small wind-and-react Tl-1223 coils. We have developed an insulation process consisting of dip-coating a thin, approximately 10-15µm, MgO layer on non-heat-treated tape. Pancake coils are then tightly wound on an alumina former (greater than 40 turns with 8mm internal diameter from an overall length of 4-5m of tape), and given a final heat treatment before the former is removed. We have also fabricated a stack of 3 pancake coils connected by resistive silver **joints** to give a total length of more than 10m. These coils were given a final sintering heat treatment of 840°C for 8h. Smaller coils of about 0.5m were given a final melt processing heat treatment. We **have not** observed any degradation in Ic values in short samples MgO coated in the same way, so we do not believe that the reaction conditions are greatly altered by the coating.

Coil properties

The measured Ic values of whole coils were found to be significantly lower than those measured in short sections of the tape. As we have previously observed that the self field generated by the tape can limit the measured Ic in short tapes, we have also investigated this self field effect in small coil geometries. The value of Ic measured in the inner section of the *small coil* varies by 20% for different current contact positions. These results show that even in a small coil the measured Ic is reduced as the number of turns through which the current flows (and the self field) increases.

We have also measured the magnetic field behaviour of Ic at 77K and 4.2K in some of the larger coils. Figure 11 shows that the behaviour observed at 77K for a single pancake coil and a 3 pancake stack with a total length of more than 10m is very similar. These tapes show typical behaviour for weakly linked Tl- 1223 tapes with a rapid decrease in Ic for small fields up to 0.1 T with no further significant decrease until the field exceeds around 5T. Measurements taken at 4.2K have shown that Ic decreases relatively slowly in fields of up to 15T. We believe that these are the first tests on long Tl- 1223 tapes in high magnetic fields, and they reveal the intrinsic superconducting properties of polycrystalline 1223 materials are very well reproduced in tape samples [7].

Conclusions

We have investigated each stage in the processes required to fabricate superconducting coils from Tl- 1223 superconducting material; including powder synthesis and composition, mechanical processing, the relationship between microstructure and superconducting properties and strategies for achieving grain alignment in order to optimise a process route. A novel melt process for Tl- 1223 tapes has been studied in detail. We have also investigated the technical aspects of coil fabrication and measured the properties. of some demonstrator coils over a wide range of magnetic fields. Engineering critical current values over 3,000 Acr^{e-}2 have been reproducibly achieved, and demonstrator coils more than 10m in length have been tested in high magnetic fields.

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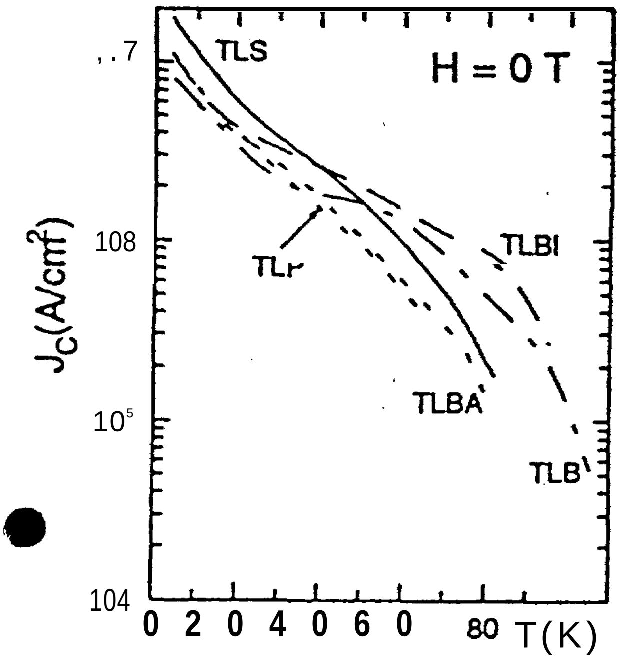

Figure 1 Temperature dependence of intra-granular Jc at zero applied field.

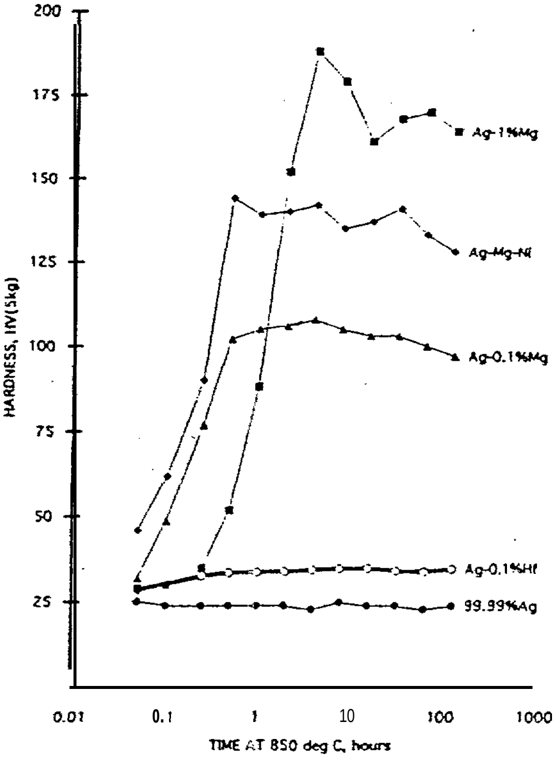

Figure 2 Hardening response of bulk silver alloys at 850°C.

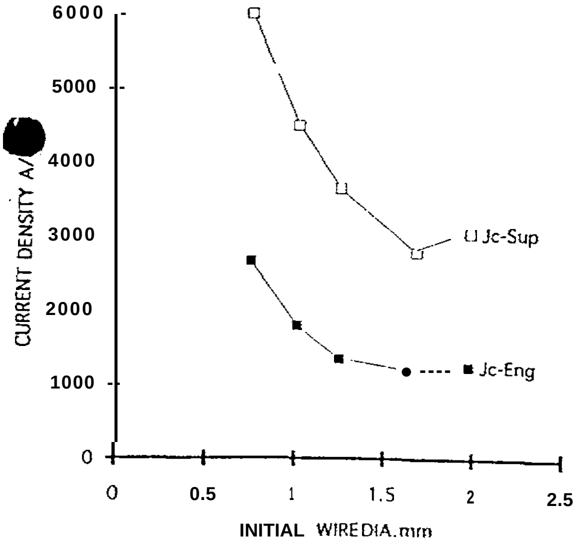

Figure 3: I Variation of Jc with different starting diameters (TlBi).

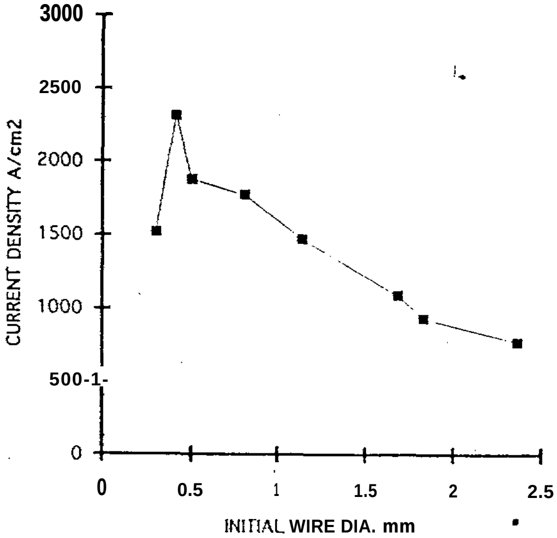

Figure 3b Variation of Jc with different starting diameters (Tl Pb).

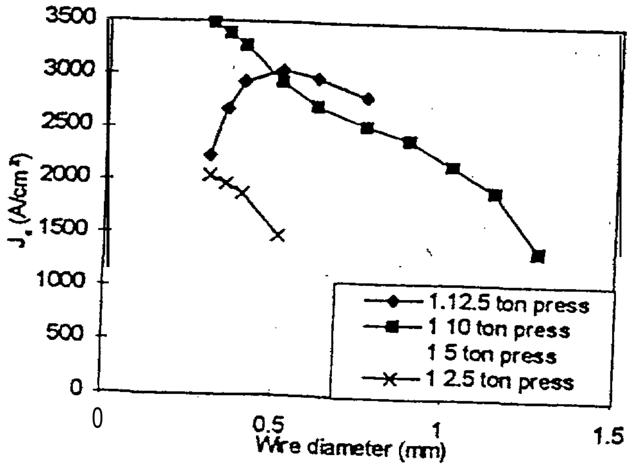

Figure 4 Effect of increasing pressure on E-Jc (TlPb).

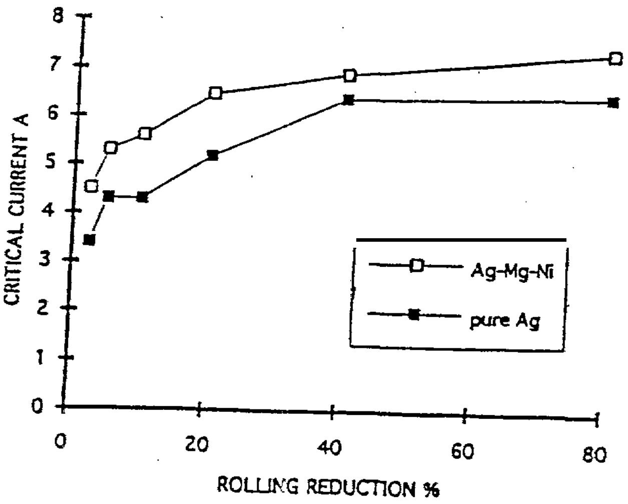

Figure 5 Increase in critical current with rolling reduction (TlBi).

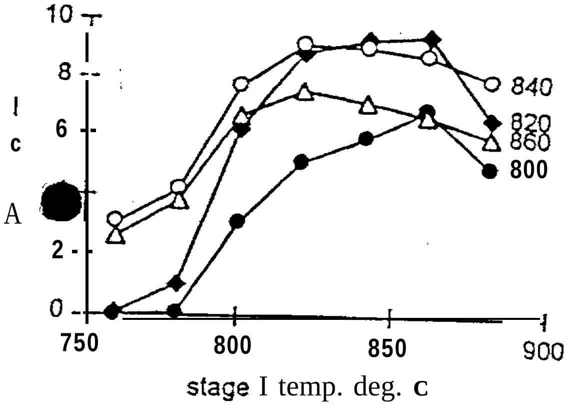

Figure 6 Determination of optimum annealing temperature for 2 stage process (TlBi).

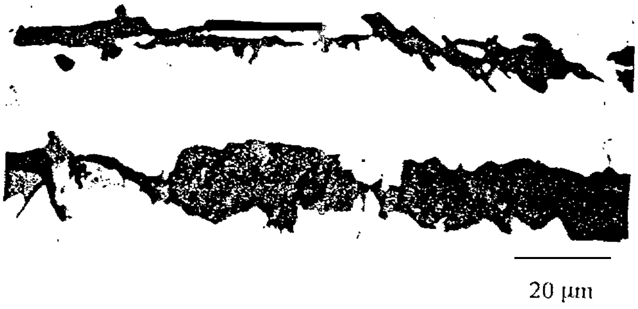

Figure 7 Light micrograph of a multi-filamentary tape showing some grain alignment in thin section.

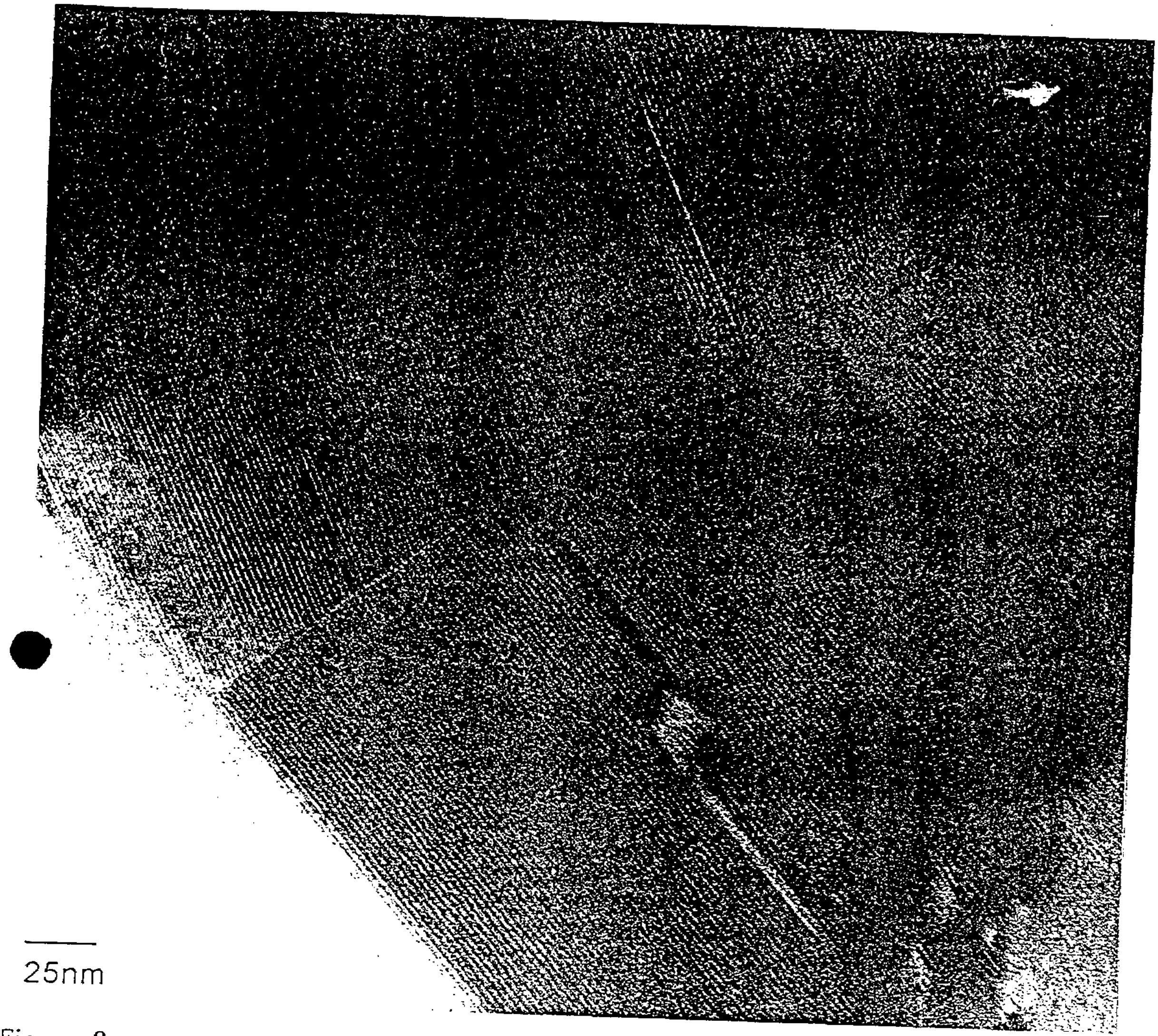

Figure 8 - TEM micrograph showing examples of the clean grain boundaries in the Tl-1223 tapes.

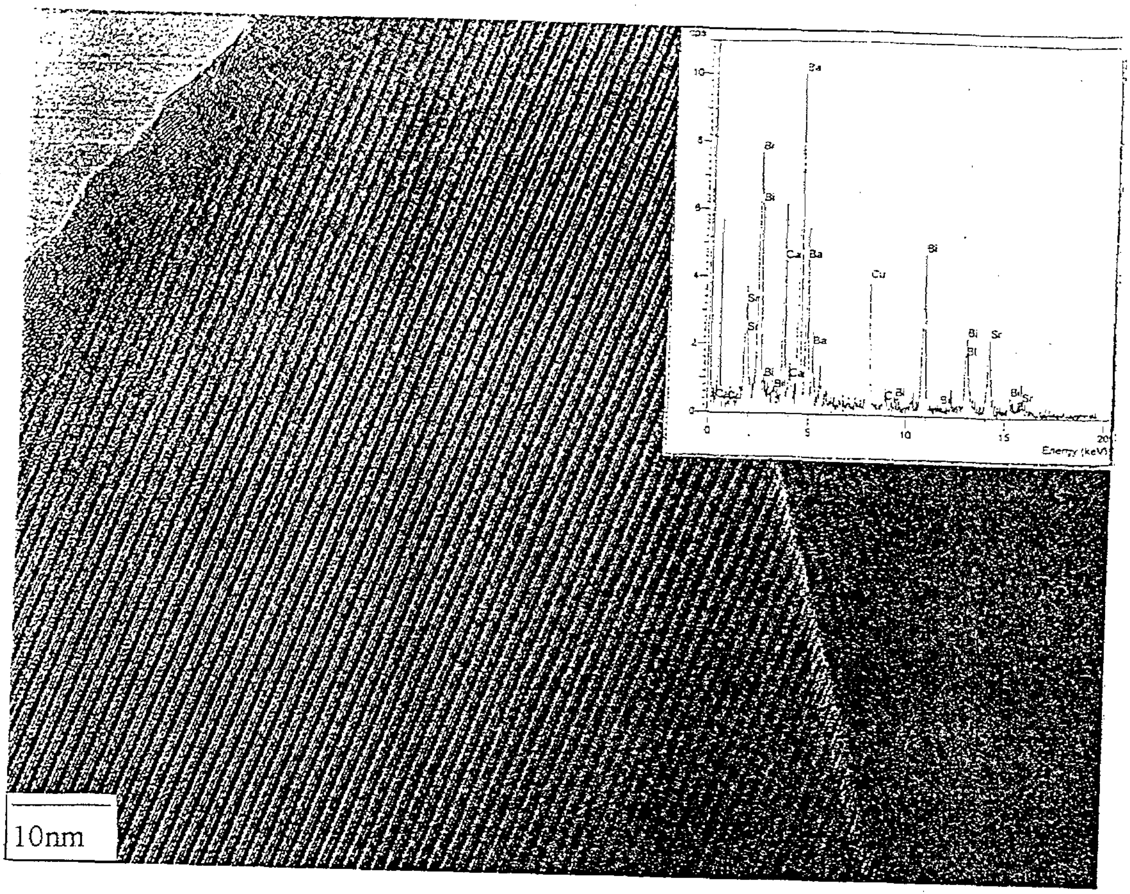

Figure 9 TEM micrograph with EDX pattern showing a particle containing Ba-Sr-Bi-Ca lattice fringes associated with a layered structure.

with

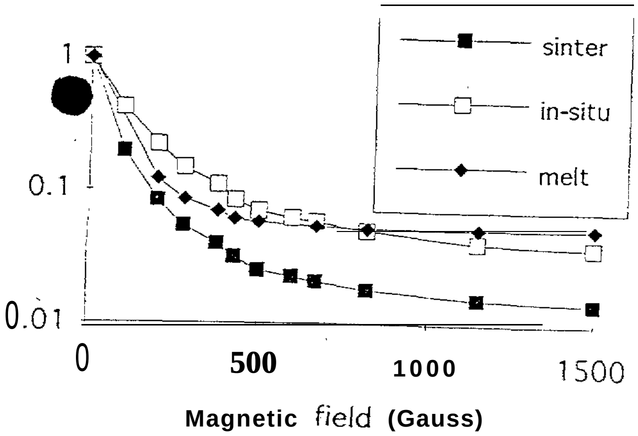

Figure 10 Effect of applied magnetic field on Ic values for tapes made using different processes

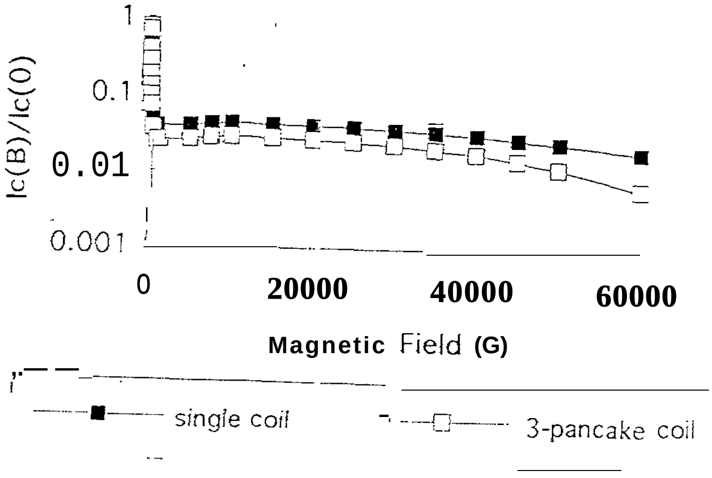

Figure 11 Ic measured in applied magnetic fields for a single coil and a 3 pancake coil stack

Preparation of highly textured YBaCuO tapes by electrodeposition

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Abstract

We have shown that it is possible to prepare extremely textured YBaCuO tapes by a combination of sequential electrodeposition of “metallic” precursors and heat treatments. Although the Tc values of our tapes are around 82K, 8 to 10 degrees lower than that reported for good quality YBaCuO, we have recently achieved a very respectable transport Jc value of 8,500 A/cm^2 at 77.4 K. We believe that pollution with S or Cl from the electroplating baths is responsible for the low Tc values of our tapes, and that reducing the level of contamination will allow us to significantly increase both Tc and Jc values in these YBCO tapes.

Introduction

A combination of electrodeposition and subsequent heat treatments offers a preparation process for complex materials which is simple, cheap and well adapted to mass production of ‘tapes in a continuous manner. Encouraging results on the electrophoretic deposition of HTS materials have been reported in the literature, but usually with submicron powders which are delicate to prepare and very sensitive to contamination [1-5]. In electroplating, matter is also transported by an electric field, but the force is applied to ions which are several orders of magnitude smaller than the particles used in electrophoretic processes. The various ionic species required to synthesise a given superconductor can be deposited simultaneously or sequentially. Simultaneous deposition is a *priori* more attractive because it allows mixing of the species at the atomic scale, and needs only a single deposition step. However, in the case of YBaCuO, the deposition potential of copper is so different from those of yttrium and barium that very soon only copper is deposited if complexing agents like cyanides are not used [6]

Alternatively, sequential deposition does not permit very intimate mixing but makes the control of the relative amounts of the various ions deposited rather simple, and is much more appropriate to mass production. Moreover, since we have already patented a process for the production ofBi-2212 HTS tapes which consists of alternating sequential deposition and heat treatment steps [7-9], it was an obvious extension of this earlier work to try to prepare YBaCuO tapes via art electrodeposition route.

Technical description

50 mm thick silver tapes 20 mm in width were used as substrates for electrodeposition of our precursors. As received from Goodfellow, the cold rolled tapes are rather rough on the micron scale. In addition to longitudinal scratches due to the roughness of the rolling cylinders used, the surfaces of the tapes are heavily cracked. Since we have. in mind to deposit YBCO layers of a few micrometers in thickness, it is quite clear that these tapes have to be smoothed. This can be done either by diamond polishing or by annealing at high temperature. The former technique gives better results but is tedious and would significantly increase the production cost of the tape, whereas the latter is fast and cheap. Hence we have focused our work on annealing. A typical area of a silver tape annealed at 870°C for 15 minutes is shown in Figure 1; most of the initial defects have disappeared, although they are replaced by grain boundary and twin boundary grooves plus facets, both being less severe defects than the rather deep initial cracks.

Selection of the electrolytes

Copper plating is very thoroughly documented, hence we used one of the baths recommended in the literature, namely: 1 Mole of $CuSO_4, 5H_2O$ + 0.5 Mole H_2SO_4 in distilled water with platinum anodes and a current density of 30 mA/cm^2. The copper deposition efficiency determined by Inductive Coupled Plasma analysis (ICP) and confirmed by weight measurement was found to be 100%, as expected.

The few publications which deal with yttrium deposition mention that this element is difficult to deposit, and most of them report that the deposit is in fact a heavily cracked layer of yttrium oxide [10- 12]. Because of its high negative deposition potential, yttrium cannot be deposited from an aqueous solution. Hence an organic solvent with a very broad potential stability domain must be used. We have experimented with: dimethylsulfoxyde (DMSO), dimethyleformamide (DMF), ethanol, methanol, acetone and acetonitryle (AN). As' yttrium salts, we tried nitrate, bromide, chloride, iodide and perchlorate compounds. It was found that few of these can be substantially dissolved in any of the solvents. After a large number of experimental conditions were investigated, the best results were obtained with: 0.2 Mole of $Y(NO_3)_3.4H_2O$ in DMSO stabilised with $Y(OH)_3$ using platinum anodes and a current density of 15 mA/cm^2

Because the Y salt used was not anhydrous, some water was introduced into the electrolyte which dissociates under the high negative potential applied to the cell. This gives rise to proton generation and a gradual decrease of the pH of the electrolyte with a consequent reduction in the yttrium deposition rate. In order to keep the deposition rate constant, so as to control the amount of yttrium deposited, we stabilised the pH of the electrolyte with yttrium hydroxide. ICP analysis 'revealed that the deposition efficiency of Y was not perfect, but around 80%.

Barium plating is even less documented than Y, but since Y and Ba have very similar deposition potentials we tried the same solvents and the same salts. Reasonable- results were obtained with:

O. I Mole $BaCl_2.2H_2O$ in DMSO, stabilised with $Ba(OH)_2$
0.1 Mole $BaBr_2.2\ H_20$ in DMSO + AN, stabilised with $Ba(OH)_2$
0.1 Mole $Ba(ClO_4)_2.3\ H_20$ in DMF, stabilised with $Ba(OH)_2$

all using platinum artodes and a current density of 15 mA/cm^2. ICP analysis has shown that Ba was deposited with a 100% efficiency from all these baths.

Nature and thermal evolution of single element deposits

Copper

It was verified by electron microprobe analysis that the deposit of copper was really pure metallic copper- Micrographs of Cu deposited for 10 seconds on diamond polished silver (Figure 2a) and on annealed, silver (Figure 2b) clearly show that the roughness of the deposit is very, dependent upon that of the substrate. Apart some spots where Cu is missing due to incorrect rinsing, the deposit of Cu on the diamond polished silver tape is smooth, very fine grained and homogeneous in thickness. By contrast, the Cu layer deposited on the annealed silver tape has bigger grains which are distributed very heterogeneously, suggesting that the nucleation of Cu is very sensitive to the orientation and the microstructure of the Ag grains.

In air or in oxygen copper is quickly oxidised as the temperature is increased. We have shown by Differential Thermal Analysis (DTA) and thermogravimetric measurements (TG) that rapid oxidation of Cu begins at about 300°C in oxygen, and that CuO does not react with Ag at least up to 925°C. It was observed that dense metallic copper gradually transforms into CuO powder. The sintered CuO grains are rather well separated and already of about 0.5µm in average size after the Cu deposit was introduced and maintained in air for 15 minutes in a furnace heated to 870°C. For longer duration or higher temperatures, the grains are coarser and the silver backing is visible between them.

Yttrium

Y deposits were not grey as expected for a metal but transparent, both during deposition and when removed from the bath, rinsed and dried. It was deduced from XPS analysis that the dried deposit was in fact yttrium oxide with a very thin yttrium carbonate top layer. Moreover this layer is heavily cracked, and since silver is uncovered in the cracks they appear as black bands in scanning electron micrographs, Figure 3. As for copper, the mass of the Y deposit was proportional to the deposition duration. Since Y_2O_3 is strongly insulating, further deposition is only possible in the cracks where the silver substrate is uncovered. It was observed that if a second Y deposition is performed after removing the specimen from the bath and drying it, the amount of this element which can be deposited saturates after about 1 minute. However, if the deposition is stopped and the specimen kept in the bath for 5 minutes before Y deposition is re-started, the mass of Y deposited remains proportional to the deposition duration. This indicates that in the bath the deposit is a reasonable electrical conductor. Our interpretation of these observations is that yttrium is deposited not as metal but as hydroxide and that this hydroxide rapidly transforms into oxide when removed from the bath. Moreover, it is very likely that the cracks are not present in the bath during deposition but appear when the hydroxide layer transforni into oxide, for if cracks were present in the bath yttrium would deposit in them as it does when it is re-deposited on a cracked specimen.

The major consequences of this behaviour are that cracks can be refilled by a short Y re-deposition, or that other elements like Cu or Ba can be deposited in the unrefilled cracks of the Y_2O_3 layer. However, when the cracks are refilled further deposition cannot be performed unless the surface is covered with a metallic layer by a technique other than electrodeposition.

Barium

A typical barium deposit is neither grey nor metallic. It is white and it consists of hydrated barium hydroxide, which slowly transforms into barium carbonate in open air, as determined by XPS analysis. In optical microscopy (Figure 4) the layer appears to be well crystallised when the deposition is performed under optimum conditions. We have shown with DTA + TGM and electron microprobe analysis that under oxygen, barium hydroxide transforms into barium oxide and peroxide. According to the Ba-O equilibrium phase diagram, BaO and BaO_2 melt in an eutectic manner at about 800°C [13]. We did observed our Ba deposit was melted after 10 minutes annealing in flowing oxygen at 820°C giving rise to a very dense and textured layer. The barium based layers are always very insulating, hence further electrodeposition on them is not possible.

Thermal evolution of binary systems

copper-barium

Using the procedure described above, a barium layer was deposited on top of a copper one, in the atomic proportion 2 Ba for 3 Cu. The various specimens prepared in this way were annealed under a range of different conditions. We determined from DTA that barium and copper oxides start reacting to form solid $BaCuO_2$ grains at about 650°C. If the heating rate is Very slow, all the BaO and BaO_2 are consumed before they reach their eutectic melting temperature, leading to a porous specimen sintered in the solid state. On the contrary if the heating rate is fast enough, free BaO and BaO_2 melt and react with the CUO giving rise to a dense and textured layer sintered in the presence of a liquid phase. At about 900°C the eutectic melting of CuO and $BaCuO_2$ occurs, and the silver is strongly de-wetted. The result is a lot of small islands of black $BaCuO_2$+CuO on a silver surface.

Copper-yttrium

To investigate the behaviour of the binary 'system Y_2O_3-CuO, the yttrium layer was deposited on top of the copper one, in the atomic proportion of 1Y for 3 Cu. The' various specimens prepared were annealed under different conditions up to 925°C. We determined from DTA that yttrium and copper oxides start reacting to form solid $Y_2Cu_2O_5$ grains at about 850°C. The major difference with the Ba and Cu oxides is that the eutectic melting of "Y and Cu oxides occurs at 108O*C, and consequently at 925°C the reaction occurs in the solid state leading to a porous small grained material. When complete, it leads to a mixture of 2.5 CuO moles for 1/2 $Y_2Cu_2O_5$ moles. Longer annealing or treatment at higher temperatures just coarsens the structure, but does not allow the Y_2O_3 film to completely transform into the blue $Y_2Cu_2O_5$ phase. Since Cu oxidation transforms the continuous Cu layer into an agglomerate of CUO grains, the interface between the Y_2O_3 and the Cu layers suffers a large stress when [illegible]per is oxidised, which could explain why the Y_2O_3 layer loses its adherence to the underlying CUO.

yttrium-barium oxides

To investigate this system, barium was deposited in the cracks of a Y_2O_3 layer and annealed at various temperatures. It was found that the reaction between these two oxides is only significant above the eutectic reeking point of BaO and BaO_2 at about 800°C, leading to the formation of an intimate mixture of small needle like grains of Y_2O_3 and a Ba-Y-O composite not identified. With refilled Y_2O_3 cracks and the use of a silver sputtered layer, the reation was 'more homogeneous. To explore the symmetric case, Ba first and Y next, we have annealed the barium layer and then made it conductive by sputtering of a silver layer before depositing yttrium. The same kind of microstructure was observed, but since silver was partially de-wetted by the melted Ba layer, the result was not homogenous.

Thermal evolution of the ternary system

To synthesise YBa_2Cu_3O, we have deposited the 3 elements Y, Ba and Cu and annealed the samples under various conditions. Since we can perform intermediate annealing to fix the deposited layers and also makes them conductive by auxiliary metallisation, there is a complete flexibility in our choice of the order of deposition.

Cu, Y,Ba sequence without intermediate annealing

As explained before, because of the presence of cracks it is possible to deposit Ba *on* the Y_2O_3 layer. Hence, to make the process as simple as possible, in our first attempts, we tried to avoid any intermediate annealing and used the sequence (X,-Y, Ba without refilling the :racks of the Y_2O_3 layer. Whatever the heat treatment performed to synthesise YBaCuO, *the* 'esistive transition was very broad and incomplete. This was because some parts of the yttrium leposit peeled off when the sample was dipped into the Ba deposition bath. To avoid [his 'roblem we have co-deposited Y and Ba on Cu. After optimisation of the heat treatment we got ither good samples exhibiting a sharp resistive transition (2K) but with an onset at 82K istead of 90 K for high quality YBaCuO. Nevertheless the transport critical current density, :. was 3,500 A/cm^2 at 77K in zero applied field.

The advantage of co-deposition is that Ba and Y are intimately mixed, but the drawbacks are that the layer is cracked [Figure 5) and that some parts of it peel off during heat treatment before reacting with the underlying CuO. Moreover it was found to be very difficult to obtain a deposit with a homogeneous Y/Ba ratio over the whole surface.

Cu, Y,Ba sequence with intermediate annealing

When an intermediate annealing is performed after the Y deposit, if the cracks are not refilled, Ba can be deposited in the cracks of the Y_2O_3 layer, just as in the previous case, but this time since the islands of Y_2O_3 adhere to the underlying CUO layer they do not peel off. Because BaO and CuO fill the crack networks, when they melt their eutectic Liquid, which wets the Y_2O_3 islands, has a tendency to dig a groove during the final heat treatment. Hence if the cracks are too widely separated, the initial network of cracks is replaced by a network of dewetted silver.

Since the distance between the two ridges of the cracks depends on the thickness of the yttrium layer, on the current density used to deposit this layer and on the intermediate heat treatments, the optimisation of the process to get non-dewetted YBaCuO tapes was rather delicate and took a lot of time and the preparation of a very large number of samples. Figure 6 shows ‘tie surface of a typical high quality specimen, with excellent phase purity and uniformity.

It was observed that the longer the duration of the annealing the bigger the grains, the stronger the texture and the higher the transport Jc values. However, even though these specimen were annealed at 450°C in oxygen for 24h the typical Tc values were rather low: 84K. The transport Jc of these specimens was about 4,400 A/cm^2 at 77K in zero applied field. Since the texture is not perfect, 28% of the yttrium is missing, the cracks are only partially smoothed and the Tc is Iow, we concluded that it should be possible to improve this result quite substantially. To try and increase Jc, we re-adjusted the Y content of the material. For reasons which are not yet clear complete re-adjustment to the precise YBCO 1:2:3 stoichiometry lead to smaller grains and lower Jc values. However, partial stoichiometry re-adjustment was beneficial and has permitted us to achieve a Jc value of 6,600 A/cm^2 at 77K in zero applied field with a Tc onset of no more than 82K.

Since the most probable reason why our Tc values are low is incorrect oxygen stoichiometry, we look for pollution with species able to substitute for oxygen. Because DMSO is known to generate SO_4^{--} ions which react with Ba to form $BaSO_4$, we have taken EPMA X-ray intensity maps of the sulphur distribution. From these ‘maps and local analysis, we have determined that barium sulphate was really present as small precipitates which coarsened during long annealing {Figure 7). Though $BaSO_4$ is very stable, it is possible that sulphur substituted YBaCuO is also stable, and since it has been shown in the literature that substituting S for O lowers Tc [14-15], sulphur pollution could well be responsible of our low Tc values. Consequently we tried to replace DMSO by a sulphur-free solvent. DMF was found to give good deposits with $BaClO_4$ but we have established that this salt introduce chlorine contamination which is also well known to lower Tc values. Moreover, we have determined that when Ba is deposited with DMF and Y with DMSO, the final sample is still sulphur polluted.

When the cracks of the Y_2O_3 layer were refilled as described above it proved impossible to deposit Ba in an homogeneous way. Hence a metallic layer of Cu or Ag was sputtered on the surface and annealed under vacuum before performing 13a electrodeposition. On this adherent copper layer the deposit of Ba was rather homogeneous and using this procedure we finally got crack-free samples. Since the layer was smoother, its texture was stronger as shown by the very highly aligned XRD pattern in Figure 8. Presumably because this specimen prepared with the $BaClO_4$ salt, and so was polluted with chlorine, its Tc value was even lower; 80K.

However, despite the proximity of Tc to the temperature of Liquid nitrogen, the transport Jc at 77.4 K was 4,100 A/cm^2.

Y, Cu, Ba sequence with one metallisation and intermediate annealing

Our interpretation of the extensive set of experiments presented above is that YBaCuO nucleates and starts to grow in the presence of a liquid phase the composition of which is nearly that of the eutectic between BaO-BaO$_2$-CuO plus a small amount of Y$_2$O$_3$. As a result, we thought the samples could be improved by;

(i) Y plating
(ii) to refill the cracks in the Y deposit
(iii) next to make the surface metallic with sputtered Cu
(iv) and finally to deposit Ba.

An additional good reason to try this deposition sequence is that the Ba and Cu liquid oxide is expected to wet the yttrium oxide layer better than the silver one . However to take advantage of this effect, it is necessary that the Ba and Cu oxides melt before they react with the underlying Y$_2$O$_3$ layer. Consequently, optimisation of the process requires us to find the correct temperature profile to apply, and in particular the best temperature ramp rate. There was insufficient time in the project comprehensively to investigate all the parameters in the heat treatment schedule, but our preliminary results are" very promising; already the 123 grains are substantially larger than in earlier samples.

Preparation of thicker layers

When our specimens with unrefilled cracks in the Y$_2$O$_3$ layer were annealed at 920°C, the 123 grains were much bigger but the silver substrate was severely de-wetted. Hence to take advantage of the big grains which are presumably more perfect than the smaller ones, we have tried to re-start the procedure in order to refill the region where silver was de-wetted and to prepare thicker specimens. Because silver is more conductive than 123 at room temperature, most of the new deposits were concentrated on the silver denuded zones, leading to a complete coverage of the salver substrate at the end of the second sequence. Though the layer was not smooth and the Tc was still low (82 K), the transport Jc value we achieved was 8,500 A/cm^2 at 77K. Work is still in progress to try and increase Jc values and the thickness of the layer.

Conclusions

We have shown that it is possible to prepare extremely textured YBaCuO tapes by a combination of sequential electrodeposition of "metallic" precursors and heat treatments. We believe that the texture is good because the 123 grains nucleate and start to grow in the presence of a liquid phase. When this liquid is too abundant or present for a too long duration it de-wets the silver substrate; hence control of the, abundance of this liquid phase is the key point for getting good samples.

Although the Tc values of our tapes are around 82K, 8 to 10 degrees lower than that reported for good quality YBaCuO, we have recently achieved a very respectable transport Jc value of 8,500 A/cm^2 at 77.4 K. Since we have determined that our specimens are polluted with impurities like sulphur or chlorine which substitute for oxygen, we believe this pollution is responsible for the low Tc values of our tapes. We believe that reducing the level of contamination will allow us to significantly increase both Tc and Jc values in these YBCO tapes

Acknowledgements

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Figure. 1: Surface of the silver tape annealed for 15 minutes at 870°C in air

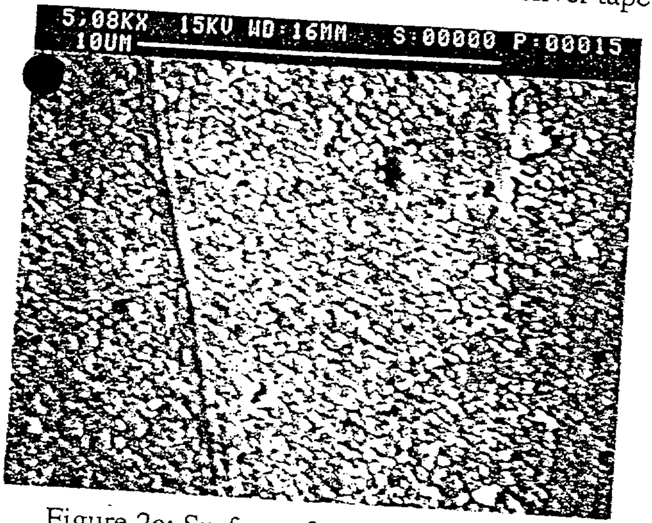

Figure 2a: Surface of a Cu layer
for 10 seconds on a polished silver tape

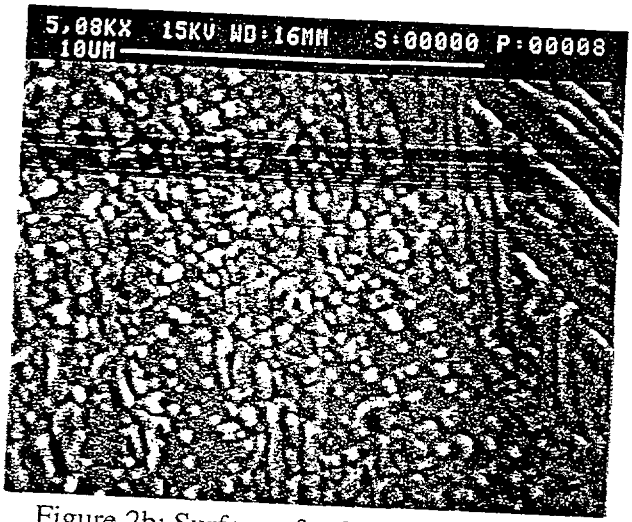

Figure 2b: Surface of a Cu layer deposited
deposited for 10 seconds on a silver
silver tape heated for 15 min at 870°C

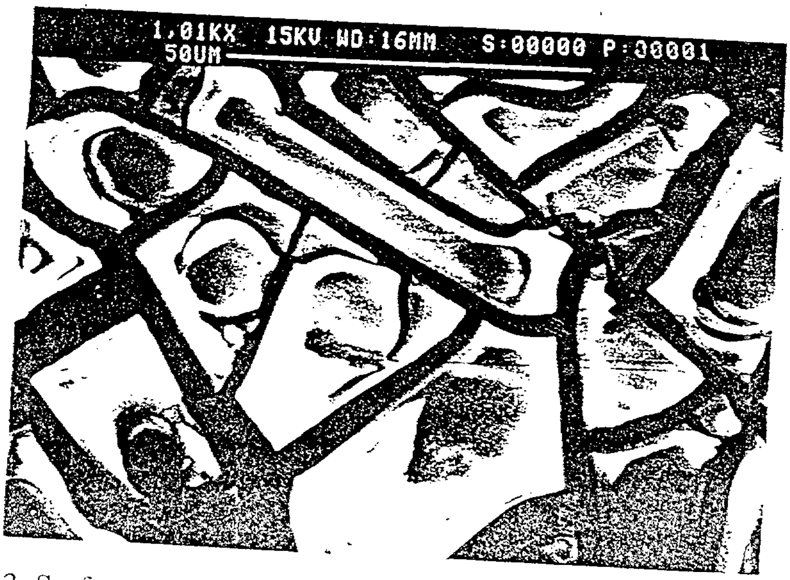

Figure 3: Surface of the cracked Y layer deposited for 60s at 2.5 A/cm^2

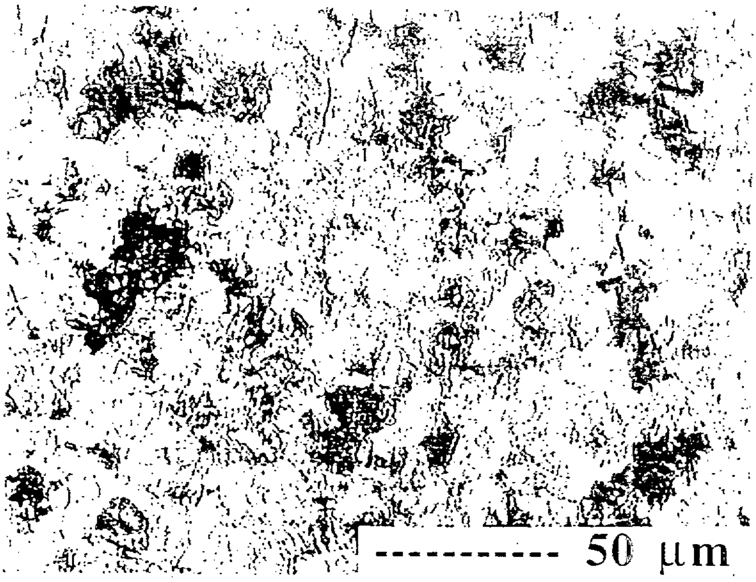

Figure 4: Surface of a fresh as-deposited barium hydroxide layer.

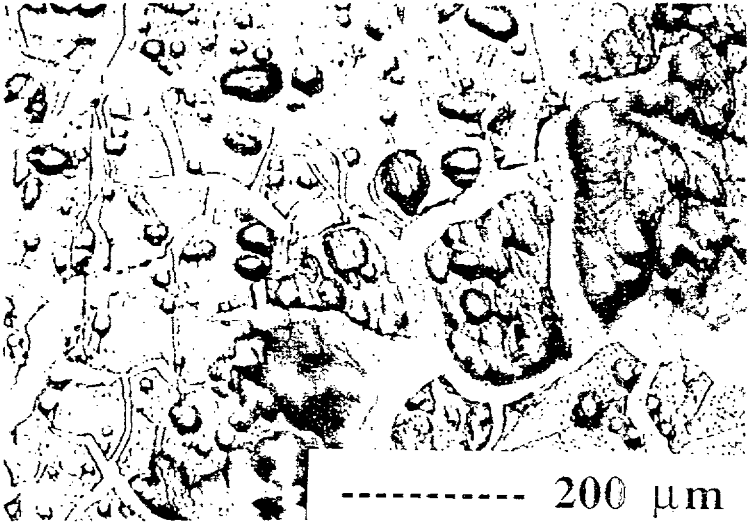

Figure 5: Surface of a co-deposit of Y and Ba on Cu.

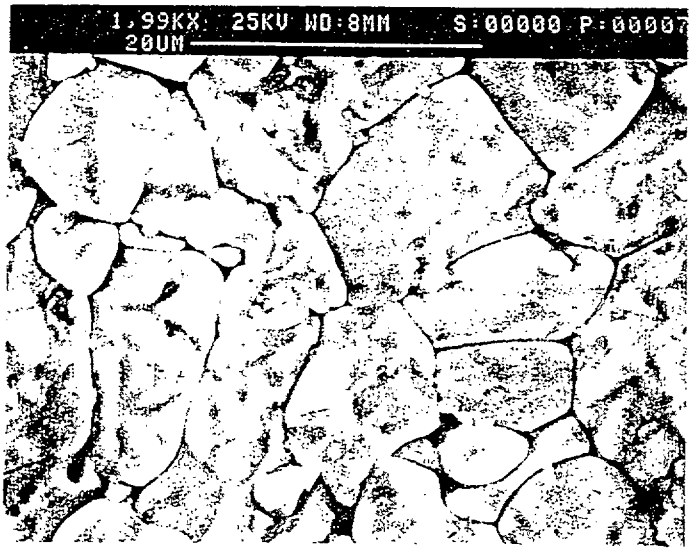

Figure 6: Surface of non-dewetted $YBa_2Cu_3O_x$ sample annealed for 100 h at 910°C in flowing oxygen.

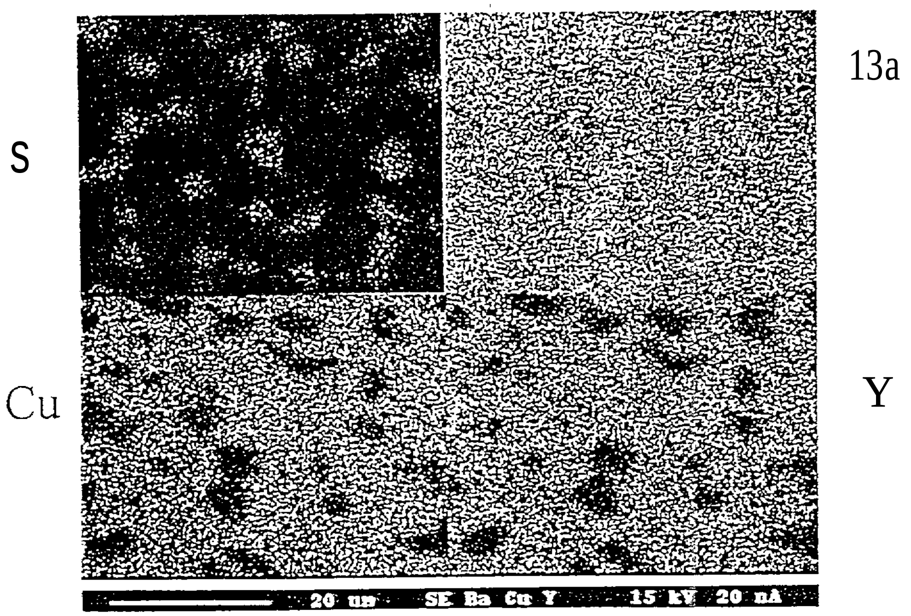

Figure 7: EPMA X-ray intensity maps of S, Ba, Cu and Y.

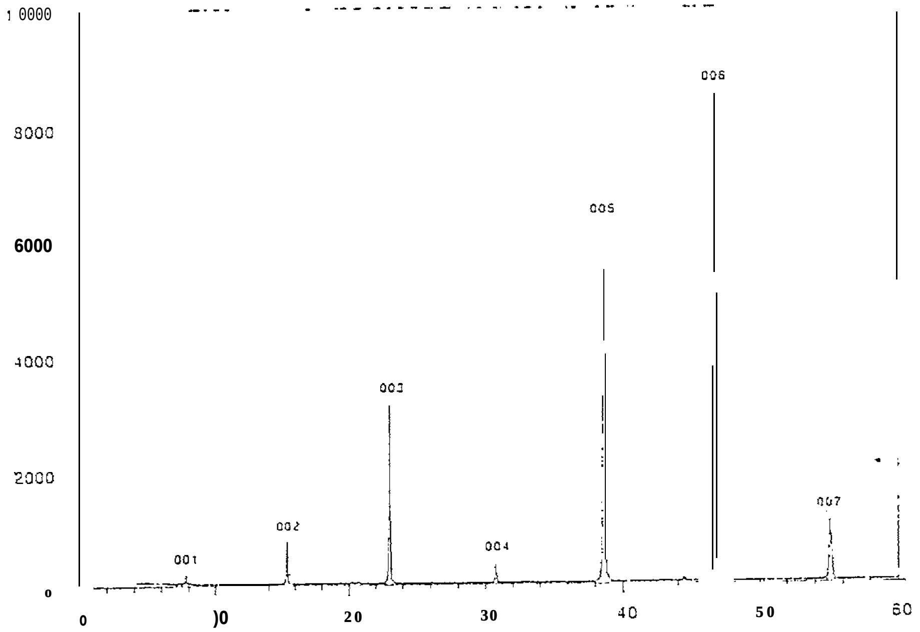

Figure 8: X-ray diffraction pattern of a specimen prepared by refilling the cracks in the Y_2O_3 layer.