Review of the application of high temperature superconductors in coated conductor development and the measurement of their properties.

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Abstract - *Since the 1960s, Nb-Ti, exhibiting a superconducting transition temperature Tc of 9K, and Nb_3Sn, with a Tc of 18K have been the materials of choice for superconducting applications. The prospects for the future changed dramatically with the discovery of ceramic high temperature superconductors exhibiting Tc values well above the boiling temperature of liquid nitrogen (77K). These materials are now widely considered for large power applications, electronics and magnets including a.o. power transmission cables, motors, generators, fault current limiters, transformers, NMR and MRI.*
The fabrication of useful conductors out of these layered cuprates encountered some problems in areas such as chemical and structural purity, stability, oxygen stoichiometry and weak links. However, a first generation of silver sheathed composites based on $Bi_{2-x}Pb_xSr_2Ca_2Cu_3O_{10}$ has already been commercialised. It is now a widespread view that superconducting wires with high performance under strong magnetic fields and at elevated temperatures above liquid nitrogen, will need to be realised using the $(RE)Ba_2Cu_3O_y$ materials. Because of the weak link nature of these materials, a second generation of biaxially aligned coated conductors was developed. As a consequence, many deposition techniques have been studied to grow thin films of the superconducting $(RE)Ba_2Cu_3O_y$ and adequate buffer layers on suitably prepared textured substrates. In this paper, the critical parameters in the deposition of thin films using vacuum and non-vacuum techniques will be reviewed.
Finally, this review will address the measurement of the obtained properties of these coated conductors. The most important practical characteristic of a superconductor is its critical current density. Spectroscopic methods such as I.R. play an important role in the development of adequate precursors for chemical solution deposition of thin films. Finally, microstructural analysis using XRD, SEM and TEM is important to reveal the relation of these features on the transport properties of the films.

Introduction

The growing population and the accelerated industrialisation of emerging countries require economical, sustainable and ecological utilisation of energy. High Temperature Superconductors (HTSC) can make a significant contribution in that area. Moreover, the developments in molecular biology and life sciences over the last years indicate that instrumentation will play an important role in medical and clinical practice, where, through the application in NMR and MRI, HTSC magnets can play an important role.

Since the discovery of oxide superconductors in 1986, research in the material science field proceeded and may efforts for the development of the conductor technology corresponding to many industrial superconductivity applications have been undertaken.

The first generation HTSC wire technology for practical applications was the oxide-powder-in-tube(OPIT) deformation processed wire. It consists
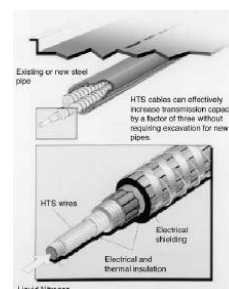

Fig. 1 : HTSC cables produced with OPIT process

of a composite of fine filaments of Bi-2223 in a silver or oxide-dispersion-strengthened silver matrix. These wires are prepared in the form of a tape, several millimetres wide and a few tenths of millimetre thick and are now being manufactured by a number of companies[1-5]. Although mechanical properties of these wires are reasonably robust and engineering Jc values have reached more than 10^3 A/cm^2 at 77K and at commercial lengths, there are several weak points in this system in that high critical current density cannot be attained under a high magnetic field in the range of liquid nitrogen temperature. Therefore, recent developments in the second generation coated conductors, where a thin film of (RE)Ba$_2$Cu$_3$O$_y$ superconductors is deposited on an appropriate substrate, with specifications required by the specific application, gain a lot of interest. The reasons for the development of this second generation tape are multiple. With a 1 MA/cm^2 current density, a one micron thick layer of YBCO could carry 100 A of electrical current at 77 K in a 1 cm wide strip. Since the current increases in proportion to the width, the industry standard for characterizing performance in these wires is to divide the current by the width of the wire, which in this case gives 100 A/cm-width. With either a 3 micron thick layer or 3 MA/cm^2 current density, the electrical performance would jump to 300 A/cm-width. Converting these performance numbers to the industry standard 0,4 cm wide HTS wire, typical for first generation wires produced today, one obtains a performance of 120 A in a 0,4 cm wide tape. This performance level is close to that of commercial HTS wire and is a key commercial target for HTS cable wire. Further increases in thickness or current density, or finding a way to incorporate two layers of YBCO in a single wire architecture would then give performance exceeding first generation by a significant margin at 77 K. Another important advantage is the possibility of achieving commercially viable in-field electrical performance at higher temperatures. The reason for this lies in the irreversibility line, which is the limit of superconductor critical current density in the magnetic-field/temperature plane. At any given magnetic field, the irreversibility line of YBCO lies at much higher temperature than that of BSCCO-2223, fundamentally because of the different coupling between adjacent sets of Cu-O planes in the atomic structure of these materials.

The overall goal is to develop robust, reproducible and economic processing technologies leading to high performance coated conductors. A three dimensional grain alignment of the superconducting layer is necessary to attain full material characteristics because of the large anisotropic properties of the RE-Ba-Cu-O structures. This requirement has to be satisfied in long tapes for applications of the coated conductors. This paper will review the various techniques that were developed to obtain three dimensional texturing.

Generic HTSC coated conductor manufacturing techniques

The basic film architecture can be described as a flexible metallic substrate with a thickness of about 25µm, covered by a relatively thin buffer layer (10nm - 100nm) and a superconducting layer of a few microns. Future technological applications in practical devices put
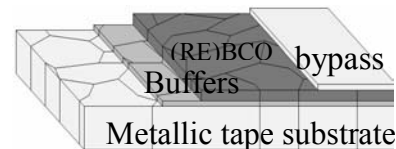

Fig. 2 : Schematic view of a coated conductor

additional requirements to the architecture of tapes such as (i) the provision for protective end-capping layers intended to function as quench protection, electrical insulation, stress relief and passivation to corrosion, (ii) the provisions to be made for the preservation of flexural strength at small bending radius and the mechanical forces to be endured locally under the generation of exceedingly high magnetic fields and thermal cycling. In addition, it has to be borne in mind that the overall performance of such a multi-layered composite, in terms of critical current density, will increase dramatically if the non-

superconducting fraction of the cross section of the film is as low as possible, thus increasing the engineering critical current density.

It is commonly believed that good film orientation, minimisation of grain boundaries and prevention of interdiffusion are some of the important parameters to achieve high critical current density Jc.

In the early developments, most of the experimental research focused on thin film deposition on single crystal dielectric substrates, using physical deposition techniques such as laser ablation, sputtering and evaporation. The resulting films were not suitable for applications such as coils, magnets and power transmission lines. More recently, efforts have been directed to grow HTSC films on flexible metallic substrates.

In general, the development of a coated conductor will consist of the following operations :
- preparation of appropriate substrate material
- deposition of buffer layer(s)
- deposition of HTSC material
- optimisation of required thermal treatment
- finishing layers (passivation, insulation…)

Techniques for preparing appropriate substrates / buffer layers

A number of properties are related to good quality substrates for the deposition of textured layers :
- they must provide a suitably textured surface to promote the required ordered growth of the HTSC crystals so that only low angle grain boundaries result.
- this implies that the substrate lattice parameters are compatible with the deposited thin film.
- the mechanical properties of the substrate should be adequate : it should be flexible, possess a high strength and have an expansion coefficient similar to that of the deposited thin film.

Silver would be the material of first choice as a substrate for YBCO because it neither oxidizes nor reacts with the superconductor. The textures of Ag that are suitable for coated conductor applications are the cube texture {100}<001>, {100}<011>, {110}<110>, and {110}<001>. Doi et al.[6] reported that out of the four possible cubic Ag textures, NdBCO would only grow on {100}<001> texture while YBCO would only grow on {110}<110>.

There has been intensive research on Ag as a possible coated conductor substrate. However, it has several drawbacks including low melting point (931 °C in air), high raw material cost, and poor mechanical properties. Moreover, it is difficult to keep the desired texture, especially at high temperatures. Toshiba Corp. recently reported a 100-m long of Ag-0,1wt%Cu/Ag-10wt%Ni/Ag-0.1wt%Cu clad tape with improved strength. Up to 1 m of the tape has been deposited with YBCO directly without buffer layer by PLD with YBCO in-plane FWHM of 23°. The average transport Jc reported was 0,12 MA/cm2 with Jc above 10^5 A/cm^2 throughout the entire 1 m length. The higher material cost of Ag over Ni and Ni-alloy tapes may be compensated by the elimination of additional processing steps for buffer layers.

Similar reinforced Ag composite ribbons have also been developed by Suo et al.[7] They examined the possibility of using AgMg, Ni, or Ni alloys as a reinforced core for Ag tapes and succeeded in producing {110}<011> Ag tapes with Ni core having in-plane FWHM of 10-15°. A very thin Cu intermediate sheath was used in between the Ag outer layer and the reinforced core in order to improve the bonding between the two layers prior to deformation.

For the moment, Ni and Ni alloys are considered as standard substrate materials as it is well known to form a good cube texture easily.

Two processes for producing metallic substrates are currently being used. In the Rolling Assisted Biaxially Textured Substrate (RABiTS) process the starting metal strip is hot rolled and annealed to promote a textured surface. The best texture quality with nearly absent none textured grains is achieved in NiW (4-5 at%) composite materials[8-9]. This material possesses a high yield strength of ~ 200MPa and reduced magnetisation losses.

In the Ion Beam Assisted Deposition (IBAD) technique, no texture is forced in the metal substrate but the first buffer layer deposited on the metallic substrate is forced to have a preferred texture, independent of the underlying metal substrate. Here, the biaxial texture is achieved by means of an ion gun that orients the growing oxide buffer layer while it is being deposited onto the polycrystalline metallic substrate [10]. The deposition in a continuous reel-to-reel system of highly oriented MgO has been realised using this technique [11.] Hasteloy is the preferred choice of substrate because of its good thermal expansion match with the buffer and (RE)BCO materials. The IBAD process is an extremely slow process.

Finally, a third route, Inclined Substrate Deposition (ISD) is one of the competing techniques of the previous ones to affect a good alignment, and has been neglected for quite a while against RABiTS and IBAD. By inclining the substrate with respect to the orientation of the plasma plume during oxide deposition, a comparable degree of texture can be achieved [12].

Techniques for depositing buffer layers / HTSC thin films

Buffer layers prevent a destructive chemical reaction between the metal alloy and YBCO and transfer the alloy's texture to the YBCO, correctly aligning its crystalline units to enable it to carry high amounts of current. Buffer layers should also possess similar qualities to substrates : good lattice match (to the substrate and other buffer layers/HTSC layer) and equivalent thermal expansion. Also important is the structure of the interface lattice plane between layers. A general rule seems to be that epitaxy is relatively easily achieved for a larger lattice misfit if successive layers have the same structure. However a closer lattice is necessary if the crystal structure changes at the interface, for instance from rocksalt to spinel, fluorite or perovskite. The choice of buffer layer materials is based on these qualities and the oxygen diffusion coefficient to prevent uncontrolled oxidation of the Ni-alloy, the stability temperature range and the scope for "low cost" production.

Yttrium Stabilised Zirconia (YSZ) was the focus in the early studies of IBAD buffer since its lattice parameters are a reasonable match with YBCO. The YSZ texture was found to be developed gradually and only reached the desired alignment at a thickness of 1 μm. Even though early work by Iijima et al. [13] show poor buffer in-plane FWHM values of about 30°, however, Jc values of the YBCO deposited were in the order of 0,5 MA/cm2.

Improvements have been made over the years and in-plane FWHM values of 9-15° are now achievable with a Jc of 0,76 MA/cm2 on short sample. More recently, the same workers[14] reported a 10-m long Ni-alloy tape with IBAD-YSZ buffer having in-plane FWHM of 10-20°. A YBCO layer is deposited by PLD on this buffered tape with in-plane FWHM of 9° and has an average transport Jc of 0,4 MA/cm^2.

Another suitable buffer material for IBAD process is MgO. It appears that MgO has the advantage where only a very thin film is needed in order to achieve similar texture as in YSZ. Los Alamos National Laboratory is developing IBAD-MgO buffer on up to 1-m long metallic substrates, as they claimed that only 10 nm of MgO (or 1%) is needed to achieve IBAD-YSZ texture, which is approximately 100 times faster. PLD YBCO films with in-plane FWHM of 4,5-10° on IBAD-MgO/Ni-alloy substrates and transport Jc of 0,1 to > 1 MA/cm^2, depending on the substrate roughness, were reported.

Despite the seemingly intensive research and positive results via IBAD route, the technique has a major drawback as being a vacuum process that may not be cost effective for industrial-scale production.

Sumitomo Electric recently reported a 10-m long YSZ-buffered Ni-alloy tape prepared by reel-to-reel ISD with Jc of 0,05-0,2 MA/cm2 throughout the tape. The tape moving speed was 1,2 m/h and the HTS deposition rate reportedly could be raised to 3 µm/min by using an industrial scale 200 W, 660 mJ laser at 150 Hz. However, the Jc of the 10-m long tape dropped below 10^5 A/cm^2 at positions corresponding to target changing, thus, reducing the "effective" length to about 4-m pieces.

The "standard buffer layer architecture" most widely used consists of $CeO_2/YSZ/CeO_2$. In recent developments, other buffer architectures have been demonstrated to possess good barrier qualities, a.o. $M_2Zr_2O_7$ (M : Gd, La)[15]; MgO [16]; $MZrO_3$ (M = Ba, Sr).

An alternative approach is to start from a NiO coated Ni-alloy tape prepared by self oxidation epitaxy (SOE) [17-19]. The NiO layer has a rocksalt structure, with an 8.3 mismatch to YBCO. Various buffer layers can be deposited on top of this NiO layer, such as MgO and TiN, with rocksalt structure; $MZrO_3$ (M = Ba, Sr) and $Ca_{1-x}Sr_xTiO_3$, with perovskite structure; Nd_2CuO_4 with spinel structure.

The techniques used to form epitaxial buffer layers and superconducting layers can be divided into two classes : physical deposition and chemical deposition. Besides the technique involved in depositing the material, and transmitting the energy necessary for vaporisation and deposition, the major differences in the physical and chemical techniques relate to :
-    the starting material (precursor or (RE)BCO/buffer material itself)
-    the thermal decomposition, oxidation or other chemical reaction taking place
-    whether the deposited material needs post-annealing for physical and chemical transformation.

Coined as "physical methods", Pulsed Laser Ablation, Electron Beam-Based Deposition, Magnetron-Beam Based Sputter Deposition and Thermal Evaporation have been used for the deposition of ceramic coatings with specific electric, magnetic, optical and mechanical properties and some of these are in the process of reaching commercial and industrial status. A highly readable overview on the vacuum-based growth of high-Tc thin films has appeared recently[20].

However, obtaining uninterrupted deposition at high speed, increasing flexibility in composition and in film thickness, attaining independence of geometric constraints are areas in which many vacuum techniques will need sustained development in order to answer industrial demands. The development of the next generation of deposition methods, which could alleviate some of these shortcomings and which are based on deposition under atmospheric environment and from aqueous precursor materials, presents therefore a real challenge for the community of solid state chemists.

Pulsed laser deposition (PLD)[21-22]
PLD is one of the most predominant techniques used in the fabrication of HTSC coated conductors and it has produced (RE)BCO with high critical current density. In this technique, a laser beam from a source outside the deposition chamber is focused onto the (RE)BCO target and materials are ablated by the laser to form a plume. Material is then deposited onto a heated substrate. PLD has two intrinsic problems : it requires an expensive and difficult to handle vacuum system and the high power UV laser is expensive to run.

Thermal evaporation[23-24]
Substrates are mounted into a vacuum deposition chamber and thin films are deposited at pressures around 10-5-10-6mbar and high temperatures.

Chemical vapour deposition, CVD[25] *and metal-organic chemical vapour deposition, MOCVD*[26-27] These techniques make use of deposition after thermal decomposition of mixtures of sufficiently volatile inorganic or metalorganic precursors. Their usability for deposition of HTSC was demonstrated at a very early stage. They are strongly dependent on the intrinsic and relative stability of the volatile metalorganic precursors. In particular, the difficulty in finding suitable Ba-compounds, which exhibit a high tendency to polymerise, has somewhat hampered its successful application in the formation of multi-element coatings of ceramic superconductors.

It comes as no surprise that deposition from gaseous precursors under relatively higher pressure, yet better, from liquid or solid precursors could alleviate many of the objections mentioned above. In view of the technological requirements put to the composite structures described in the previous chapter, the difficulties to be encountered in such alternative media may seem enormous. However, recent results obtained by many researchers exploring this line of attack lead us to believe that non vacuum based deposition methods may prove to be a viable route to the industrial development of the future generations of coated conductors.

Because of the very high concentration of the active precursor species during deposition, in comparison to any of the vacuum-based or gas-based deposition methods, the rate of growth of the film can be many orders of magnitude higher. On the other hand, as the growth mechanism of the deposited layer is probably better described as a co-operative sedimentation phenomenon rather than the "atomic layer by layer" process encountered in vacuum and gas based techniques, difficulties in ordering and texturing of crystalline phases might be anticipated. However, our results on the deposition of CeO_2 buffer layers and NBCO superconducting layers from aqueous precursors on single crystal substrates and on textured metal tapes [28], lead us to believe that the subsequent thermal treatment, may be able to resolve those difficulties. The use of liquid media renders these techniques ideally suited for continuous coverage of very large areas of suitably pre-treated substrates exhibiting complex shapes. In its simplest form, one could envisage a single pass equipment in which a continuous tape is transported through a bath in which temperature and composition should be monitored and continuously adjusted, followed by in-line thermal treatment and subsequent operations such as passivation, lamination and slicing. The diversity in chemistries is so large that we anticipate no serious restrictions in the number of elements expected to be present and the plethora of successful experimental situations already available in the literature suggests that the presence of controlling chemicals can be completely eliminated in the final product by suitable post treatment, at least as long as organic agents and thermolabile volatile inorganic reactants are used (mostly ammonia and water). Finally, the use of gels finds its rationale in their ability to immobilise large concentrations of different ionic species together with molecular or atomic resolution in the medium under deposition, thereby ensuring maximal homogeneity in composition and distribution to the final layer. Segregation, which is difficult, if not impossible to avoid in low viscosity liquid media exhibiting sedimentation of solids, is evaded here using several strategies: the formation of a network polymeric and/or polymetallic species, in situ formation of accompanying polymers during the drying phase or the addition of polymers or gellifying agents in the so-called sol-gel process.

The term 'sol-gel' is an abbreviation for 'solution-gelling' which denotes its principle: a solution starting from precursors which are dissolved in a liquid phase, is transformed to the solid state through a sequence of chemical reactions which involve polymerisation at ambient temperatures.[29]

Sol-gel, also known as wet-chemical, processing of ceramics can refer to a multitude of reaction processes which employ a wide variety of chemical precursors to prepare many different products[30] According to Kakihana, there are essentially three different kinds of sol-gel routes: (a) colloidal sol-gel route; (b) inorganic sol-gel routes and (c) organic sol-gel routes.[31]

Colloidal Sol-Gel Method

This route involves the dispersion of colloidal particles The sol is converted to a gel by controlling the electrostatic or steric interactions between the colloidal particles. [31-33]

Because the interparticle interactions in those sols are dominated by physical forces such as Van Der Waals forces, electrostatic forces and Brownian motion, the colloidal sol-gel method is called a "physical" gel route.
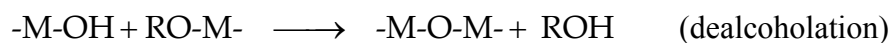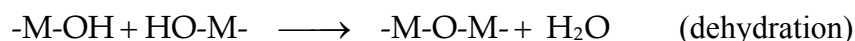
Inorganic Sol-Gel Method

Inorganic polymeric oxide gels are made basically in two ways: either from metal alkoxides in organic solvents or from metal salts dissolved in aqueous or organic solvents and stabilized by chelating ligands.[31] In both cases, the chemistry is dominated by the high electropositive character of the metal cations.

A. Alkoxide gel method[34]

Metal alkoxides have the general formula $M(OR)_z$ where M is a metal ion, R is an alkyl group and z is the valence state of the metal. On addition of water, the metal alkoxides readily hydrolyze as follows:
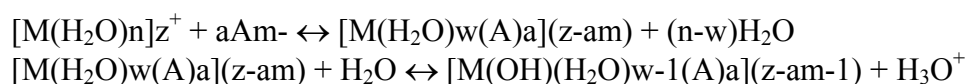
$$M(OR)_z + x\ H_2O \longrightarrow M(OH)_x(OR)_{z-x} + x\ ROH$$

Hydrolysis is followed by condensation to form –M-O-M- bonds via either dehydration or dealcoholation:

$$\text{-M-OH} + \text{HO-M-} \longrightarrow \text{-M-O-M-} + H_2O \qquad \text{(dehydration)}$$
$$\text{-M-OH} + \text{RO-M-} \longrightarrow \text{-M-O-M-} + ROH \qquad \text{(dealcoholation)}$$

In case of the preparation of multi-metal-oxides, both self-condensation (i.e. formation of -M-O-M- bonds) or cross-condensation (i.e. formation of -M-O-M'- bonds) may occur.[35] By these condensation reactions, an inorganic polymeric oxide network is built up progressively.

B. Metal-Chelate Gel Method[31, 34]

Another way to trap the randomness of the solution state is to use precursor solutions that can be converted to an amorphous glassy state when the solvent is removed. The basic idea behind the metal-chelate gel formation method is to reduce the concentration of free-metal ions (mostly hydrated in aqueous solutions) in the precursor solution by the formation of soluble chelate complexes.

$$[M(H_2O)n]z^{+} + aAm- \leftrightarrow [M(H_2O)w(A)a](z-am) + (n-w)H_2O$$
$$[M(H_2O)w(A)a](z-am) + H_2O \leftrightarrow [M(OH)(H_2O)w-1(A)a](z-am-1) + H_3O^{+}$$

From this point of view strong chelating agents such as citric acid and ethylene-diamine-tetra-acetic acid (EDTA) are preferably used in the synthesis of multi-metal oxides which greatly expands a range of experimental conditions such as pH of the solution, temperature, and metal concentrations where gelation can occur upon evaporation of the solvent. The high viscosity prevents precipitation of metal-chelate complexes and on further dehydration a clear gel forms. On cooling, the viscous dehydrated gel undergoes a rubber to glass transition and converts to a brittle polymer glass.[36]

Hydrolysis of metal ions in aqueous solution and its government by ionic charge, initial metal ion concentration and initial pH have been described in[37.] The equilibrium corresponds to the equalization of the mean electronegativities of the reaction products and theoretical calculations allow adequate choice of optimum conditions for the stepwise co-condensation of aqua-complexes (by olation) to hydroxo- and subsequently to oxo-complexes (by oxolation) in the continuously concentrating medium. The addition of other organic or inorganic complexants (ethylene diamine tetra-acetic acid, EDTA or NH_3) may again be used to lower the hydrolysis rate by competing with water molecules around the precursor ions. One must appreciate that during the drying of the gel deposited onto the substrate, continuous increase in the total metal ion concentration as well as in the concentration of pH controlling agents occurs. Based on such understanding, the path taken by a gel containing a rare earth metal,
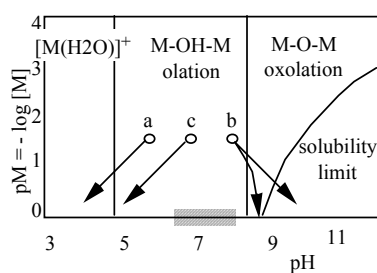
can be summarised as given in the accompanying graph (figure 3) where three cases are illustrated. Starting from point a, the gel approaches a region in which the acidity is too high to allow significant olation or oxolation.

Figure 3: Schematic representation of the path followed by a drying gel medium made up of metal ions in the presence of chelating agents. The protective use of ammonia is illustrated in the alternative path followed by point b. For further details, see text.

This is only possible from a starting point represented by b or higher in pH. Starting from c (pH above 7) could be dangerous because the solubility boundary of the chelate-complexes could be crossed, but the use of ammonia (which volatilises slowly because of the heat applied during drying) keeps the kinetic stability of the gel under control.

Organic Sol-Gel Method

The third sol-gel route involves formation of an organic polymeric network. This can be carried out in two ways. The first is an 'in-situ' polymerization route where the gel network is made by polymerization of organic monomers. If this is carried out in the presence of metal ions, it can be expected that all metal ions are homogeneously distributed into the organic polymeric network. When the process is a combination of metal-chelate complex formation and an 'in-situ' polymerization, the process is called *"polymerized complex method"*.

The second route involves the preparation of a viscous solution system containing metal ions, polymers and a suitable solvent and the process will be simply called *"polymer precursor method"*.

In general, the fabrication of ceramic oxides by the sol-gel approach involves four basic steps: (i) synthesis of the precursor solution; (ii) gel formation; (iii) low-temperature heat treatment

for drying, pyrolysis of organic species and formation of an amorphous oxide; (iv) higher temperature treatment for densification and crystallization into the desired oxide phase.

From our previous results[38] it is clear that a lot of solution parameters have a large influence on the precursor gel characteristics. Special attention has to be paid to the appropriate choice of metal source and complexans. For a good combination of these starting materials, the metal to complexans ratio and the pH of the solution also have a large influence on the formation of the precursor gels. Both parameters have to be chosen high enough to be able to synthesize homogeneous clear gels. At the other hand, these parameters should not be too high, to avoid a large decrease of mass during the thermal decomposition. As stated in the previous paragraph, hydrolysis of metal ions in aqueous solution and its government by ionic charge, initial metal ion concentration and initial pH have been described in theoretical models . From the point of view of the Partial Charge Model, equilibrium corresponds to the equalization of the mean electronegativities of the reaction products. These theories allow adequate choice of optimum conditions for the stepwise co-condensation of aqua-complexes (by olation) to hydroxo- and subsequently to oxo-complexes (by oxolation) in the continuously concentrating medium. It has been shown by us[38] that adequate buffer layers of CeO_2 can be produced based on an appropriate nitrate/citric acid system. NdBCO superconducting layers could be developed using acetate and triethanolamine systems.

TFA-MOD process for the synthesis of (RE)BCO[39]
In this method, trifluoro acetic acid produces a fluorinated precursor film. The idea behind the process is to expel the carbon content during calcinations. Drawbacks from this method are the use of relatively expensive trifluoroacetates as starting precursors and the generation of HF during the calcinations process.
Izumi et al [40] reported Jc values up to 3.6 MA/cm^2 at 77K and in self field and Ic values of 291 A for YBCO on a CeO_2 cap layer on IBAD GZO buffers. Obradors et al [41] have demonstrated the development of YBCO/CeO_2multilayers exhibiting Jc up to 1.6 MA/cm^2.

Spin coating and dip coating deposition techniques
Both methods are ideally suited[42] for the exploitation of the versatility of the sol-gel methods described above.
Spin coating is a technique with wide applications in the silicon wafer industry and it benefits from the ability to impart a spreading action on the film by control of the speed of rotation of the substrate. Obviously, flat rectangular or disk shaped substrates are to be batch processed here. Dip coating, on the other hand, is naturally suited for continuos deposition and allows great flexibility in the control of the thickness (through control of tape speed, viscosity or concentration). We have demonstrated[43] that reasonably smooth CeO_2 buffer layers with a thickness of 20-30 nm and with better than 98% [001] crystallographic orientation, could be obtained by dip coating Ce-nitrate precursor solutions onto a textured nickel tape with a speed of 1mm.min^{-1}. This also underlines the notion that the use of sol-gel techniques is not only applicable to the deposition of the superconductor layer alone but that several steps in the formation of the final tape-composite can be integrated using dip coating.
Other techniques exploited to deposit the sol gel precursors are a.o. screen printing, ink jet printing and spray pyrolysis. Deposition of superconducting systems based on Y, Bi, and Tl on the standard array of static single crystal substrates have yielded critical currents in excess of 10^5 A.cm^{-2} at 77K in self field[44]. Simple nitrate or acetate solutions have been nebulized using piezo-electric sonnicators to yield in- plane aligned YBCO films on single crystal substrates and on (110)-oriented Ag[45] with promising critical current densities > 10^4 A/ cm^2.

Another 'chemical' process that is 'liquid assisted' is hybrid liquid phase epitaxy. This technique has been exploited by several authors as alternative for deposition of buffer layers and superconducting layers [46-47].

Characterisation of the properties

A thorough investigation of chemical reactions and structure related to the precursor solution / gel systems requires the application of a range of complementary characterisation techniques. Important techniques include optical light microscopy, Scanning electron microscopy (SEM), X-ray diffraction (XRD), Infra-red spectroscopy (IR) and differential thermal and thermogravimetric analysis (DTA/TGA).

One of the most important properties of a coated conductor is the capability of carrying current and the determination of the critical current density, Jc.
Recently, the creation of artificial pinning centres in the HTSC materials for enhancement of in-field Jc, has gained a lot of interest. Matsumoto et al [48] reported the introduction of one –dimensional Y_2O_3 nano-islands. The introduction of nano-YBCO particles are also intensively studied [49-50].

Figure 4: Measurement of the bi-axial texture of a CeO_2 buffer layer using the EBSD technique

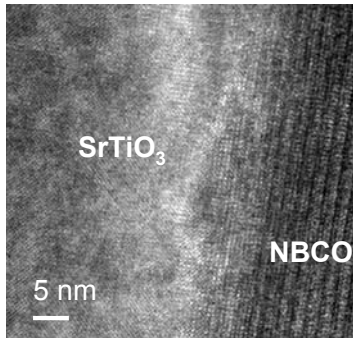The required microstructure of a coated conductor is highly demanding; continuous km lengths of bi-axially textured stoichiometric YBCO have to be deposited on a strong flexible substrate tape. Only low angle grain boundaries are acceptable with boundary angles less than about five degrees, because high angle grain boundaries present an insulating barrier to current flow. The biaxial texture and microstructure of HTSC thin films is usually determined using a combination of XRD and ϕ-scan monitoring, EBSD, TEM, SEM and AFM.

Figure 5: TEM image of a NBCO thin film grown by the sol gel technique

There are three components to the percolation problem, (i) the characteristics and properties of individual grains and grain boundaries, (ii) the microstructure, texture and grain morphology, and (iii) the macroscopic geometrical constraints such as conductor size and shape.

Conclusions

After reviewing specific advantages of the broad range of liquid-based techniques that are becoming rapidly available for the deposition of high temperature superconducting coatings on a variety of substrates, we must conclude that the time is ripe to step up their effective and systematic exploration as alternative candidates to the vacuum-based techniques that are being developed today for applications on an industrial scale. The list of techniques based on liquid precursors and for use under atmospheric pressure, enumerated in this review, is not exhaustive. Several other alternatives await the ingenuity of chemists and material scientists, such as doctor blading, the application of oxides by electrochemical plating, electrophoretic deposition, site-selective catalytic decomposition from liquid or gaseous precursors and controlled growth of native coatings.
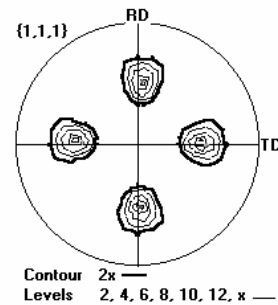
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