Nonvacuum-based deposition techniques for superconducting ceramic coatings*

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Abstract: The widespread use of vacuum-based techniques for the deposition of ceramic coatings with specific electric, magnetic, optical, and mechanical properties is well established in the research environment, and some of them have been implemented in a variety of industrial processes. However, obtaining uninterrupted deposition at high speed, increasing flexibility in composition and in film thickness, and 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, is a real challenge for the community of solid-state chemists and delineates the subject of this overview.

INTRODUCTION

Today, the deposition of a number of high-tech ceramic films on a variety of substrates is often performed using a vacuum- or low-pressure-based technique [e.g., molecular beam epitaxy, pulsed laser deposition (PLD), magnetron sputtering, metal–organic chemical vapor deposition (MO-CVD), thermal evaporation]. Many of these techniques have been applied in demanding situations such as the deposition of crystallographic textured coatings of ceramic superconductors on flexible metallic substrates. They have been extensively reviewed in several papers and books [1]. Although such techniques can be variously tuned by control over the composition and pressure of the atmosphere under which the deposition takes place and by suitable posttreatment, they are rather slow (depositing several microns per min at most), lack some versatility in the production of multi-element layers on substrates of complex shape, and are discontinuous by nature. Alternatively, the deposition of such coatings at atmospheric pressure from aqueous media presents real advantages in this respect, but this route has been much less thoroughly explored. Several methods are already available that offer a very flexible range in composition, high deposition speed, and a technological versatility that may rival vacuum-based approaches in some applications (e.g., flame spraying, plasma spraying, dip coating, spin coating, aerosol spray pyrolysis, and electrophoretic deposition). These techniques employ precursor materials that may be in the form of powders, solutions, slurries, aerosols, and aqueous or nonaqueous gels. Recently developed methods for the deposition of superconducting ceramics and their parent materials using nonvacuum-based deposition methods from liquid media will be illustrated and discussed in the following paragraphs.

VACUUM-BASED DEPOSITION

The development of electrical conductors based on high-temperature superconducting ceramics (HTSCs) has been started by several industrial groups with the aim of efficient production of energy (e.g., magnetic containment for fusion reactors), transport of energy (e.g., superconducting current leads), storage of energy (e.g., superconducting magnetic energy storage rings), control (e.g., fault current limiters, squids), and application of electrical energy (e.g., magnetic levitation, magnetic bearings, high-field NMR, superconducting electronics).

As early as 1990 [3], the development of flexible current leads based on mechanical drawing and thermal treatment of BiSrCaCuO-type superconducting powder (2212 with a T_c of 85 K and 2223 with T_c of 110 K) encapsulated in ribbons drawn from metallic silver or from Hastelloy, was demonstrated. Although their basic superconducting ingredient does not exhibit the best properties in terms of field dependence of the critical current density (see Fig. 1), its natural disposition to exhibit reasonably well-oriented bulk texture under modest mechanical pressure was rapidly appreciated. Indeed, the obstruction of the superconducting path by grain boundaries and by crystallographic misorientation of individual domain surfaces puts a high requirement on the texture inside tapes, which rely on such strongly anisotropic perovskite derivatives. Nevertheless, critical current densities, J_c, of the order of 10^4 A/cm^2 at 77 K were achieved after careful rolling and optimized thermal treatment of such composites. This "powder in tube" conductor is commercially available today [4] and has already been used to demonstrate the integration of high-temperature ceramic superconductors into the household electricity grid. However, it is obvious from the data presented in Fig. 1 that the exploitation of epitaxy upon matching single-crystal surfaces in vacuum-based deposition systems would allow a vast improvement of the quality in terms of critical current density and its concomitant magnetic field dependence. Thus, vacuum deposition of YBa$_2$Cu$_3$O$_{7-?}$ films using PLD on single crystals of SrTiO$_3$ yielded J_c values in excess of 10^6 A/cm^2 at 77 K [5]. This clearly demonstrated that the drawback of poor performance in high magnetic field associated with Bi-based oxide powder in tube (OPIT)-superconductors can be
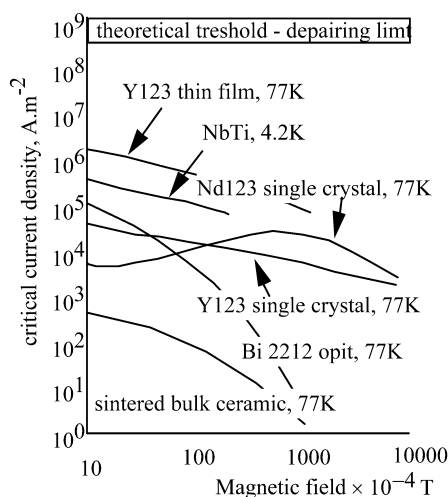

Fig. 1 Evolution of critical current density as a function of magnetic field in different classes of high-temperature superconducting materials, illustrating the general increase in performance in going from polycrystalline bulk ceramic to relatively defect-free superconducting single crystals and highly oriented thin films deposited under epitaxy by vacuum techniques on single-crystal substrates. Although critical current density for the intermetallic NbTi superconductor is relatively high, it is only usable with liquid helium as coolant and its performance drops significantly at high field. Also, notice the anomalous peaked behavior of the Nd-based materials, providing for a renewed impetus in its application for coated conductors. Adapted from Yu D'Tretyakov et al. [2].

avoided if a solution is found for the deposition of ceramic phases based on the Y-system and its rare earth analogs onto cheaper and flexible substrates. Three different methods were developed to obtain a sufficient biaxial texture in the superconducting films. After mechanical rolling and careful thermal treatment, textured metallic tapes based on Fe- and Ni-alloys were obtained (so-called rolling assisted biaxially textured substrates or RABiTS) with a thickness of about 100 μm. Alternatively, a method based on ion beam-assisted deposition (IBAD) under vacuum achieves biaxial texture by means of an ion gun that orients the growing oxide buffer layer while it is being deposited onto the polycrystalline metallic substrate. Finally, by inclining the substrate (ISD) with respect to the orientation of the plasma plume during oxide deposition, a comparable degree of texture can be achieved [6]. Such substrates and configurations have now been integrated into the vacuum-based procedures applied in many research laboratories worldwide. Coined as "physical methods", pulsed laser ablation, electron beam-based deposition, magnetron beam-based sputter deposition, and thermal evaporation have been used, and some of these methods are in the process of reaching commercial and industrial status. A highly readable overview on the vacuum-based growth of high-T_c thin films has appeared recently [7]. The basic film architecture can be described as a flexible metallic substrate with a thickness of at least 25 μm, covered by a relatively thin buffer layer (10–100 nm) in which CeO_2 and Y-stabilized ZrO_2 are the major components. This multifunctional buffer layer acts as a protective oxygen barrier for the metal substrate and as an epitaxial template for the ordered growth of the tetragonal or orthorhombic superconducting perovskite unit cell (Fig. 2). Future technological applications in practical devices put 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 multilayered composite, in terms of critical current density, will increase dramatically if the nonsuperconducting fraction of the cross-section of the film is as low as possible. Although many of these criteria and functions are not yet translated into the details of fabrication of an integrated coated conductor, the appearance of functional vacuum-based tapes in the market is expected to occur within the next five years.
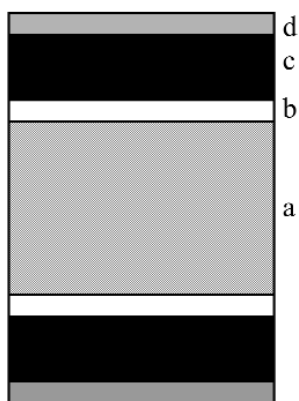

Fig. 2 Schematic cross-section (not to scale) of a flexible coated conductor, comprising a flexible metallic core with a thickness around 25–100 μm (a), coated on both sides with rare earth superconducting ceramic layers up to 5 μm thick (c) in a sandwich configuration between a protective buffer (d), and seed layer (b) based on refractory ceramic oxides exhibiting a high degree of biaxial texture and a protective end-capping layer, which may contain metallic and/or polymeric components.

NONVACUUM-BASED DEPOSITION

The necessity to deposit under epitaxial conditions and the introduction of biaxial texture by application of ion beams have favored deposition under relatively low gas pressure (10^{-4}–0.2 mm Hg). This may give rise to several disadvantages. By working under such reducing conditions, the direct formation of oxide-rich phases like the superconducting perovskites is impossible. Furthermore, the necessity for transport of material through a gaseous medium under low pressure is not conducive to high rates of deposition in the final films. Finally, the use of vacuum renders the process intrinsically noncontinuous unless provision is made to elaborate transfer mechanisms of the final film to the ambient atmosphere. In addition, methods relying on material beams (PLD, sputtering, thermal evaporation) are "line-of-sight" techniques that will suffer from geometric constraints whenever deposition on complex-shaped substrates should be envisaged.

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 nonvacuum-based deposition methods may prove to be a viable route to the industrial development of the future generations of coated conductors. At least, the combination of merits of both approaches may help to tailor the properties of conductors to their respective niches.

Once the constraint of low pressure is dropped, a broad series of methods present themselves. They will be briefly described here.

CHEMICAL VAPOR DEPOSITION [8] AND METAL–ORGANIC CHEMICAL VAPOR DEPOSITION [9]

Next to the vacuum-based deposition techniques (physical methods), several other techniques, often referred to as chemical methods, have emerged. They make use of deposition after thermal decomposition of mixtures of sufficiently volatile inorganic or metal–organic 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 metal–organic precursors. In particular, the difficulty in finding suitable Ba-compounds, which exhibit a high tendency to polymerize, has somewhat hampered its successful application in the formation of multi-element coatings of ceramic superconductors. Together with many other chemical deposition methods, they share the advantage of being relatively independent of the shape or orientation of the substrate, and the deposition process may be assisted by irradiation with laser light or RF-heating.

SOL-GEL DEPOSITION

An extensive and excellent review on the use of sol-gel deposition techniques has appeared recently [10], and it has helped to clarify and order the great variety of approaches developed over the years in this field. Although the three mainly used sol-gel methods are addressed independently in this survey, it should be borne in mind that they can be applied in several of the deposition methods described further. Indeed, the exploration of dip coating, spin coating, spray pyrolysis, ink-jet printing, and screen printing in combination with sol-gel techniques will probably provide the most fruitful line of research for future developments in this field.

A few general remarks on the use of a liquid medium and its impact on HTSC coated conductor technology are in order. Because of the very high concentration of the active precursor species during deposition, in comparison to any of the vacuum- or gas-based deposition methods, the rate of growth of the film can be many orders of magnitude higher. This is perhaps their greatest strength and attraction.

On the other hand, as the growth mechanism of the deposited layer is probably better described as a cooperative 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 recent results on the deposition of CeO_2 buffer layers from aqueous precursors on single-crystal substrates and on textured metal tapes [11], lead us to believe that the subsequent thermal treatment, which all but one (spray pyrolysis) of these methods require, 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 pretreated 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 posttreatment, 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 immobilize 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.

Alkoxide gels [12]

Hydrolysis of mixtures of alkoxides (M−OR) in nonaqueous media by the carefully controlled addition of water progressively yields polymeric species exhibiting M−O−M bonded entities after dehydration and dealcoholation. Although the reaction may be categorized as fast (seconds to minutes), it can be tuned by controlling the alkoxide-to-water ratio and by playing on environmental factors such as temperature, concentration of acid or base catalysts, and type of solvent. The major drawback associated with the formation of cuprate-type superconductors is the comparatively low sensitivity to hydrolysis of Cu-alkoxides compared to other rare earth alkoxides. The mismatch in the rate of hydrolysis can be dramatically smoothed out by the introduction of complexing agents competing with water for bonding to the metal ions. In particularly fortunate (but rare) cases, heterometallic (multiple) alkoxides can be formed of the stoichiometrically required type –M−O−M′−O−…, which result in homogeneously mixed gels as was found to be the case for $BaTiO_3$ [13]. In conclusion, the relative sensitivity to tuning of alkoxide systems is such that reduced reactivity in the precursor is to be preferred. Ample choice is provided by the following two alternatives.

Metal-chelate gels

The greatest advantage of metal-chelate gels is that their medium is aqueous from the onset. The danger of independent precipitation and segregation of the nitrate or acetate salts used here is countered by drastically decreasing the concentration of free-metal ions in solution after adding polycarboxylic acids displaying (multidentate) chelating ability and among which citric acid seems to take the lead. Hydrolysis of metal ions in aqueous solution and its government by ionic charge, initial metal ion concentration, and initial pH have been described in sufficient detail [14] to 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 (ethylenediaminetetraacetic 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 summarized as given in the accompanying graph (Fig. 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.

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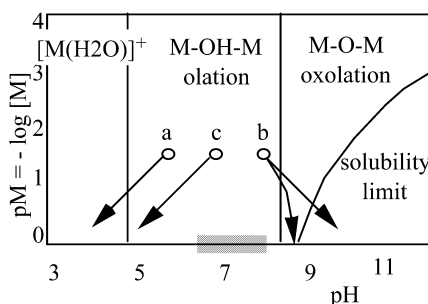

Fig. 3 Schematic representation of the path followed by a drying gel medium made up of metal ions in the presence of chelating agents. The protective use of ammonia is illustrated in the alternative path followed by point b. For further details, see text.

Pechini sol-gel and related methods [15]

In order to ascertain the immobility of ionic species, accompanying polymers can form a network in the drying solution. The addition of an excess of the same polycarboxylic acids as those mentioned before, can be readily exploited by inducing their esterification through the use of added polyalkohols (ethylene glycol is the preferred reagent). Alternatively, a separate radical polymerization can be allowed to occur, using dedicated reagents or a polymer-like polyvinyl alcohol (PVA), carboxymethyl cellulose (CMC), and other binders of that nature. If active polymerization is used, it is our experience that the continuous change in viscosity of the medium must be closely monitored for maximum benefit. Often though, the recourse to such involved mixtures of reagent components is omitted as this inevitably increases the load of organic species to be removed by later thermal treatment and generally decreases the temporal stability of the medium.

DIP COATING AND SPIN COATING

Dip coating and spin coating are both ideally suited methods [16] 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 continuous deposition and allows great flexibility in the control of the thickness (through control of tape speed, viscosity, or concentration). We have demonstrated

[17] 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 1 mm/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.

INK-JET PRINTING, MICRO-PEN PRINTING, AND SCREEN PRINTING

Such delivery systems may happily combine with sol-gel techniques. We have demonstrated at a relatively early stage of the development of high T_c superconducting ceramics, that screen printing of patterned tracks down to 100 μm width and 50 μm thickness on polycrystalline alumina was feasible [18] by exploiting the hygroscopic nature of spray-dried YBCO ($YBa_2Cu_3O_x$)-nitrate precursors, even without the use of stabilizing additives! Jet printing of Bi-2212 superconductors on polycrystalline silver tape exhibiting T_c in the range 82–92 K was also successful [19], and the implications of the integration of well-established and versatile printing technology to obtain "droplet-on-request", graded patterns and variable composition arrays lead us to envisage quite attractive implementations.

METAL–ORGANIC DEPOSITION (MOD) [20]

The MOD approach is a liquid-phase deposition technique, using trifluoroactetate precursors. After a postdeposition annealing step, good epitaxial films are obtained. J_c values in the film of 10^5 to 10^6 A/cm^2 are reported.

AEROSOL/SPRAY PYROLYSIS

The use of very short drying times in liquid droplets (10^{-3} s) in order to preserve the molecular homogeneity characteristic to the liquid phase, and to carry it over to a solid material during the rapid synthesis of large quantities of bulk HTSCs was demonstrated as early as 1989 [21]. A further development of this idea is found in the exploration of coating methods based on the spraying of aerosols onto heated substrates. The fast drying avoids the need for large quantities of controlling reagents. 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 77 K in self field [22]. 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 [23] with promising critical current densities $>10^4$ A/cm^2. As the (moving) substrate can be heated to sufficiently high temperatures, a single step and continuous deposition process is to be imagined in a strongly oxidizing atmosphere, potentially yielding very high deposition speeds or—conversely—high thickness of the order of tens of microns in seconds.

CONCLUSION

After reviewing specific advantages of a broad range of liquid-based techniques that are rapidly becoming 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 materials scientists, such as doctor blading, the application of oxides by electrochemical plating, electrophoretic deposition, site-selective catalytic decomposition from liquid or gaseous pre-

cursors, controlled growth of native coatings on dedicated alloys or solid solutions, deposition based on friction and rubbing, and even, perhaps, intelligent nanomechatronic substitution.

In view of the diversity of requirements for the complex architecture of an efficient flexible coated conductor, one may surmise that a dedicated effort from the community of solid-state chemists, physicists, and materials engineers will be required to succeed during the next decade. This pursuit is an honorable one.

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