Application of spray deposition techniques for fabrication of Sm-doped CeO₂ thin films on biaxially textured Ni-W substrate

1. Introduction

The discovery of high-temperature superconductors (HTSC) in the late 1980s dramatically changed the prospect of their use in industrial applications. They have a much higher critical temperature than metal superconductors, making it possible to use a more economical cryogen: liquid nitrogen. However, the main drawback to the broad commercial implementation of HTSCs is their high production costs; the ratio of price over performance is still not feasible when considering substituting them for conventional Cu conductors (Chen et al., 2004). To increase the feasibility of HTSCs, either their critical current density must be several times higher than that currently reached by other superconductors, or their production costs ought to fall significantly.

HTSC films are commonly produced on ceramic or metal substrates, which are thought to be reliable enough to sustain high HTSC reactivity at the elevated temperatures required for production (Fork et al., 1991). To address the issue of reactivity, chemical and thermo-resistant buffer layers of nm-thickness are commonly used between the substrate and the superconductor. The relationship between the substrate and a buffer layer is highly important, and so materials that exhibit similar lattice parameters are selected.

Several techniques have recently been developed to produce nano-sized thin films on various substrates. These can be broadly separated into two main categories, depending on the nature of

the production process: physical or chemical. The main physical deposition techniques are pulsed laser deposition (Rupp, Infortuna & Gauckler, 2006; Patil & Pawar, 2007), magnetron sputtering and electron beam evaporation (Konstantinov et al., 2000). The deposition techniques based on chemical processes include sol-gel (Konstantinov et al., 2000; De Souza et al., 2007; Petrova, Todorovska & Todorosky, 2006), chemical vapour deposition (Kumar et al., 2014; Patil & Pawar, 2011), aerosol-assisted metal-organic chemical vapour deposition (MOCVD), plasma-enhanced chemical vapour deposition (De Souza et al., 2007), electrostatic spray-assisted vapour deposition (Wei & Choy, 2005) and spray pyrolysis (Karageorgakis et al., 2011). The availability of such a wide range of thin film production techniques is explained by their growing demand in electronics applications (Chourashiya, Jadhav & Pawar, 2008).

This chapter focuses on the development of aerosol-based methods for thin film production on textured Ni(W) tapes for subsequent use as a substrate for yttrium barium copper oxide (YBCO) tapes. This method seems to be a promising and cost-effective alternative to other techniques as it does not require any vacuum conditions, and could be simply controlled within a broad range of parameters to produce films of required thickness, composition and morphology. Aerosol-based methods have demonstrated applicability in the production of nano-size particles for HTS bulk-doping (Agranovski et al., 2006), buffer layer deposition (Jiang et al., 2006; Wu et al., 1991; Dahmen & Carris, 1997) and HTS coatings (Dahmen & Carris, 1997; Knoth et al., 2006). We selected samarium-doped ceria as a suitable candidate for producing a uniformly thin film on an Ni(W) substrate because it has a good chemical compatibility and lattice matching with YBCO and textured Ni substrates (Li et al., 2008). The doping of CeO₂ with RE-oxides, such as Sm, Eu, Yb and other lanthanides significantly improves the quality and physical characteristics of CeO₂ thin films (Li et al., 2008; Zeng et al., 2006).

Several research groups have fabricated oriented CeO_2 on Si (100), glass and YSZ substrates using aerosol-assisted techniques (De Souza et al., 2007; Jiang et al., 2006; Pavlopoulos et al., 2008). However, only Wei and colleagues report the outcomes of fabrication of strongly oriented CeO_2 on biaxially textured Ni using electrostatic spray-assisted vapour deposition (We, Zhi & Choy, 2006). In the present work, we extend the research into the formation of doped CeO_2 buffer layers by using aerosol-assisted techniques such as air-assisted spraying (AAS) and ultrasonic spraying (USS). We tested aerosol deposition process parameters such as substrate temperature, distance between discharge nozzle and substrate, air carrier flow rate, solution concentration and deposition time in our efforts to achieve smooth, defect-free surfaces and biaxially oriented thin films.

2. Experiment

2.1 Materials

Cerium and samarium nitrate hexahydrate water solutions were prepared for aerosol production. $\text{Ce}(\text{NO}_3)_3$ was initially dissolved in ultrapure water ($\Omega > 18 \text{ MOhm}$) and stirred for 30 minutes. $\text{Sm}(\text{NO}_3)_3$ was then added to the solution and further stirred for another 30 minutes. The solution was then placed in an ultrasonic bath for 10 minutes to ensure complete dissolution of all precursor materials. Then the solution was diluted with H_2O to achieve Ce-Sm nitrate concentrations of 0.02–0.03 M and 0.6–0.06 M for ultrasonic and air-assisted spraying, respectively. The molar ratio of Sm and Ce in the solution was 1:4, aiming to achieve $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ stoichiometry (Lei et al., 2011).

2.2 Experimental setup

Textured Ni-5%W (Ni(W)) tapes approximately 10x5 mm in size and 100- μ m thick were used as the substrate material for this study. Prior to their experimental application, the sample tapes must be chemically cleaned to assure that trace contaminants are destroyed. This was achieved by submerging sample tapes in a sealed container of ethanol, and finally a 30 minute submersion in an ultrasonic bath of de-ionized water. To produce a Sm-doped CeO₂ thin film, a Ni(W) tape was placed on a hot plate, and exposed to an aerosol stream produced by a nebulizer for the required time. Two nebulizers were used in this research to atomize the solution described above: a 3-jet collision nebulizer (BGI Inc., Waltham, MA) and an ultrasonic nebulizer (MY-520A, GE Sci-Tech, Xinxiang, China).

The operational principle of the collision nebulizer is based on fluid suction by a compressed air stream due to reduced static pressure created by a specially designed nozzle, following inertial removal of large droplets from the air carrier as the result of their collision with the internal wall of the device. The resulting small droplets are discharged from the nebulizer, creating an aerosol stream (May, 1973). The ultrasonic nebulizer is operated by using an electronic oscillator capable of generating high frequency ultrasonic waves sufficient to produce a vapour, which immediately condenses, generating mist at the discharge point of the device. The collision nebulizer was operated at a flow rate of 6 L min⁻¹ of dry and filtered compressed air. The amount of aerosol reaching the Ni sample was controlled by the distance between the nebulizer's discharge nozzle and the Ni(W) tape. It was especially important to ensure that aerosol particles were instantly evaporated upon collision with the surface and that no visual moisture remained on the surface. Any presence of moisture could unfavorably redistribute materials on the surface,

causing uneven film thickness. For this reason, the temperature of the hot plate was kept at 200°C and 350°C for ultrasonic and air spraying, respectively. A significant decrease in temperature on the surface of tapes during air-spraying required a higher hot plate temperature and 10-s deposition intervals. The particle size distribution at the exit of both nebulizers was determined using a laser particle counter (Model 4507, Aeronanotech, Moscow, Russia) to ensure their efficient operation.

We attempted spray pyrolysis of the films (simultaneous decomposition during aerosol deposition) at temperatures >350°C. Such temperatures are often used to prepare Ce-oxide films on glass substrates (De Souza et al., 2007; Petrova, Todorovska & Todorosky, 2006; Kumar et al., 2014; Patil & Pawar, 2011; Chourashiya, Jadhav & Pawar, 2008). However, this approach produced films with poor surface quality, mainly due to significant temperature reduction and variation caused by spray-related cooling (particularly during air spraying). We discontinued this approach in the present work because the deposited films required subsequent sintering at higher temperatures for densification and appropriate texture formation.

Once deposition was complete, the sample was heat treated in a tube furnace under a flowing argon environment. During heat treatment, the sample was initially calcined at 350°C for 1 hour to decompose nitrites, then the sample temperature was increased to 900°C-1100°C (at the rate of 150°C/h) and held at 900°C for 3 hours. To prevent oxidation of the Ni(W) substrate, samples were placed within graphite linings to ensure oxygen-reduced conditions.

2.3 Materials' characterization

Decomposition of dry precursor material under conditions similar to the film calcinations and sintering was studied using differential thermal analysis (DTA) and thermogravimetric analysis (TGA) in a simultaneous thermal analyzer (Netzsch STA 449F3). To prepare samples, $\text{Ce}(\text{NO}_3)_3$ and $\text{Sm}(\text{NO}_3)_3$ were dissolved in water as described above and then dried onto a glass substrate at 100°C . After drying, the powder was placed in the DTA/TGA crucible along with a small piece of graphite and was analysed in flowing argon at a heating rate of $10^\circ\text{C}/\text{min}$ from 20°C – 950°C . This procedure ensures conditions identical to those used for heat treatment during thin film production.

Thin film phases and crystallites parameters were determined by X-ray diffraction on a Bruker D8 advance powder diffractometer with Bragg-Brentano geometry at 40 kV, 30 mA using copper K_α radiation ($\lambda=1.5406 \text{ \AA}$) in conjunction with a graphite monochromators. The surface morphology and microstructure of thin films were characterised by scanning electron microscopy with an energy dispersive X-ray spectroscopy analysis module (Philips XL-30 ESEM, accelerating voltage at 15-25 kV). The valence states of Ce and Sm in thin films, and their elemental ratio, were investigated by X-ray photoelectron spectroscopy (XPS) (Kratos Axis Ultra photoelectron spectrometer with Al K_α (1253.6eV) X-rays).

3. Results and discussion

3.1 Characterisation of aerosols

Aerosol size distributions obtained for both nebulizers are presented in (Fig. 1). As can be seen, particles produced by an ultrasonic nebulizer are slightly larger, which is quite common for these devices. Both size distributions are clearly poly disperse with the majority of particles representing sizes in the range from 1 to 4 micrometers.

Fig. 1: Size distribution of Sm/CeO₂ produced by collision and ultrasonic nebulizers

3.2 Characteristics of as-deposited films

Based on visual inspection, as-deposited films had a smooth, uniform surface of dried metalloorganic film. To identify the relevant post-heat-treatment temperatures, DTA/TGA of $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ spray-deposited dry powder was conducted in an oxygen-reduced environment. The DTA/TGA curves reveal four exothermic peaks at 100 °C, 150 °C, 200 °C and 310 °C (see Fig. 2), indicating that the decomposition of metalloorganic involves several steps before the film is fully converted to the oxide form. The latter temperature is almost the same as the decomposition temperature of Ce-nitrates in the air (Patil & Pawar, 2011; Chourashiya, Jadhav & Pawar, 2008). A small mass reduction was noted at 350 °C–450 °C, with no mass loss observed at higher temperatures.

Fig. 2: Thermogravimetric and differential thermal analysis profiles of decomposition of $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ spray-deposited dry powder

3.3 Film crystallography

Table 1 lists the fabrication parameters of films prepared by air-spray and ultrasonic-spray methods, and their crystallographic and microstructural characteristics. Highly c -axis oriented thin films were obtained using both deposition methods; however, each method was performed under different conditions and optimized to achieve textured films. Using ultrasonic deposition, textured Sm-doped CeO_2 thin films were obtained at a deposition time varying between 60 and 180 seconds, with subsequent sintering in an oxygen-reduced environment at 900°C . In contrast, films highly oriented in the $\langle 00n \rangle$ plane were obtained by air-spraying only when deposited over at least six time intervals of 10 seconds each, with intermediate heating of the sample to ensure a sufficiently hot surface for droplet evaporation. On completion of the coating, samples were sintered at 1100°C in a reduced-oxygen environment.

Table 1: Processing parameters and characteristics of spray-deposited $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ thin films

	Concentration, M	Deposition time, s	Sintering temperature, $^\circ\text{C}$	Thickness, nm	Lattice parameter, a ($\text{\AA}$)	Crystallite size, nm	Texturing, (200)/(111) ratio
<i>By air-spraying</i>							
A-1	0.06	60	1100	40	5.41	20.3	6.7
A-2	0.6	60	1100	400	5.42	26.0	1.7
<i>By ultrasonic spraying</i>							
U-1	0.03	60	900	55	5.44	21.1	4.3
U-2	0.03	60	900	55	5.42	19.6	2.1
U-3	0.03	120	900	100	5.42	24.0	3.1
U-4	0.03	120	900	110	5.42	23.8	2.7
U-5	0.03	180	900	160	5.41	29.9	3.6
U-6	0.03	180	900	160	5.42	27.3	4.7
U-7	0.02	600	900	370	5.43	11.5	0.04

X-ray diffraction spectra of textured Sm-doped CeO_2 thin films prepared by both deposition methods are shown in (Fig. 3). Small (111) peaks are observed in all samples; however, a relative peak ratio of (200)/(111) was >1 for most of the films in Table 1 (except for sample U-7). The (200)/(111) ratio in polycrystalline samarium cerium oxides (JCPDS card No. 34-0394) is typically 0.2-0.3. This observation demonstrates that the produced films have a preferred $\langle 00n \rangle$ plane orientation following texture characteristics of the Ni(W) substrate. An excessive quantity of graphite near the substrate could result from the deposition of amorphous carbon, as demonstrated in (Fig. 3a and 3b), by two humps in the X-ray diffraction pattern. Interestingly, carbon was not detected when samples were sintered at 1000°C or higher. Films produced by ultrasonic deposition did not demonstrate oriented growth in the $\langle 00n \rangle$ plane, while thin films prepared by air-spraying and sintered at 1100°C clearly demonstrate $\langle 00n \rangle$ orientation (Fig. 3c). When samples were air deposited and sintered below 1100°C , films were not textured.

Fig. 3: X-ray diffraction patterns of Sm-doped CeO₂ thin films: deposited by ultrasonic nebulizer for (a) 120 s and (b) 180 s, both sintered at 900°C, and by (c) air spraying for 60 s and sintered at 1100°C

The lattice constant, a , was calculated to be within the range of 5.41–5.44 Å, which is in good agreement with published lattice constants of Sm-doped CeO₂ thin films (Patil & Pawar, 2007; Phok & Bhattacharya, 2006). No distinctive differences were observed in the lattice parameters of the films with different thicknesses prepared by alternative deposition methods.

The crystallite size of the films, d , was calculated by Scherrer's formula as:

$$d = k\lambda/\beta\cos\Theta$$

Where $k=0.9$ (Patterson, 1939), λ is the wavelength of X-ray diffraction, β is a full width at half maxima of (200) peak, and θ corresponds to the Bragg angle. An increase in crystallite size from 19.6 to 29.9 nm was observed with increasing film thickness. These values were similar to the grain size in Sm-doped CeO₂ thin films prepared on Ni by aerosol-assisted MOCVD (Jiang et al., 2006) and electro-deposition (Phok & Bhattacharya, 2006).

3.4 Surface morphology

The surface morphology is an important characteristic of the films for subsequent deposition of HTS layers. As demonstrated in (Fig. 4a), the surface of an air-sprayed thin film deposited over 60 seconds has <00n> orientation (Fig. 4b), and was not uniform or smooth throughout the entire sample: smooth areas coexist with relatively rough surfaces. Since the deposition time during air spraying was limited due to rapid cooling of the sample, a high precursor material concentration (0.6 M) was deposited over 60 seconds, enabling thicker Sm-doped CeO₂ films. After sintering, cracking was observed on the surface of these films (Fig. 4b b). The air-spray deposition results suggest that this method should be further developed to obtain more consistent, reproducible films with uniform and smooth surface morphology.

Fig. 4: Scanning electron microscope image of Sm-doped CeO₂ thin films prepared by air spraying for 1 min from (a) 0.06 M and (b) 0.6 M and sintered at 1100°C

In contrast, the ultrasonic spray deposition procedure resulted in films with uniform, smooth surface morphology, deposited during time intervals of 60–180 seconds, which resulted in film thicknesses of 60–180 nm, respectively. The 60-nm thick film demonstrates some porosity in its surface (Fig. 5a), while the thicker films have well-packed grains of 20–100 nm (Fig. 5b and 5c). These Sm-doped CeO_2 films are still relatively thin, and grooves at the grain boundaries of Ni(W) substrate are still visible on their surface.

Fig. 5: Scanning electron microscope image of Sm-doped CeO_2 thin films deposited by ultrasonic spray for (a) 1 min, (b) 2 min, (c) 3 min and (d) 10 min, sintered at reducing conditions at 900°C

Increasing film thickness by increasing the deposition time to 10 minutes at the same molar concentration of solution led to surface cracks (Fig. 5d), similar to that observed in one of the

thick films deposited by air-spraying (Fig. 5a). The critical thickness of Ce-based films depends on the film composition, substrate material, method of deposition and heat treatment, and is reported to be in the range of 100–800 nm (Li et al., 2008; Zeng et al., 2006). For the techniques used in this study, critical thickness is mainly limited by the mechanism of the precursor decomposition, and is likely to be around 200 nm for a single deposition step. By optimizing the concentration of the solutions and substrate temperature, critical thickness could be controlled to achieve the required parameters.

3.5 Film chemical composition and Ce oxidation states

XPS analysis of the films indicates the presence of four elements on the surface, including cerium (Ce 3d and Ce 4d peaks), samarium (Sm 3d peak), oxygen and carbon. The Sm/Ce ratio in the films was estimated by comparing Sm 3d and Ce 3d XPS spectra (an area of Ce peaks including 3d 3/2, 5/2 and the satellites were calculated after subtracting the base line value). The determined Sm content, x , in $\text{Ce}_{1-x}\text{Sm}_x\text{O}_{2-\delta}$ thin films varied between 0.15 and 0.24. Similar values between 0.18 and 0.25 were determined by comparing Sm and Ce peaks in EDX spectra. These values correspond well to the molar ratio of Sm:Ce=0.25 in the precursor solution.

(Fig. 6) shows the XPS spectra of cerium and samarium in the films deposited by ultrasonic spraying for 1 minute and 10 minutes, and in films deposited by air spraying for 1 minute. To identify the ceria valence state on the surface of these films, Ce^{4+} and Ce^{3+} profiles are also plotted as dashed lines (Holgado, Alvarez & Munuera, 2000). In ultrasonically deposited samples, cerium 3d spectra in (Fig. 6a and 6b) were composed of two multiplets, which corresponded to the spin-orbit split $3d_{5/2}$ and $3d_{3/2}$ core holes. The profile of these six peaks is

typically observed in CeO_2 oxides (Phok & Bhattacharya, 2006), indicating that most of the cerium is in the Ce^{4+} valence state, despite being sintered in reduced conditions and the presence of carbon on the surface. XPS spectra of Ce in air-deposited films consists of a superposition of Ce^{4+} and Ce^{3+} profiles, indicating the presence of Ce^{3+} on the surface. This difference is likely to be associated with the sintering temperature of this sample, rather than with the deposition method, and needs to be further investigated. XPS spectra of samarium were identical in all samples, and correspond well to the Ce^{3+} valence state (Suzuki et al., 2000).

Fig. 6: X-ray photoelectron spectra of Sm-doped CeO₂ thin films, deposited by ultrasonic spray for (a) 1 min, (b) 10 minutes, and (c) air-assisted spray for 1 minute

4. Conclusion

$\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ thin films were produced on Ni-5%W substrates by ultrasonic and air-assisted spray deposition of cerium and samarium nitrate hexahydrate water solutions, with subsequent decomposition of nitrate precursor materials and sintering of oxide films, under reducing conditions in the absence of hydrogen in a neutral atmosphere. Textured films with smooth surface morphology were obtained using both techniques, and characteristics such as lattice constants, crystalline and grain sizes, Sm-doping levels and oxidation states of Ce and Sm are reported. Further studies are needed to determine the optimum film thickness and sintering procedure. However, the present results indicate that the texturing growth of thin films in $\langle 00n \rangle$ planes following Ni(W) substrate orientation can be achieved using both deposition methods.

Considering that the air assisted aerosol generation could produce slightly smaller particles, it might be beneficial for fabrication high quality films. However, a much more sophisticated setup would be required to minimize the influence of substantial cooling of a substrate. In contrast, ultrasonic generation is simple and cost effective. Regardless of the fact that the size of aerosol produced by this method is slightly larger compared to the air assisted process, it did not significantly influence the film quality, making this method more attractive for application, especially for small scale production facilities.

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