Oriented Sm-doped CeO$_2$ thin films on biaxially textured Ni-W substrate produced by ultrasonic spray deposition

1. Introduction

To develop efficient processes for fabricating CeO$_2$ thin films on substrate layers, the feasibility of low-cost methods, including spray deposition based procedures, should be investigated in more detail. This chapter reports the results of our feasibility study on the formation of $<00n>$-oriented Ce$_{1-x}$Sm$_x$O$_{2-\delta}$ thin film on textured Ni-5%W tape using an ultrasonic spray deposition technique, and discusses the characteristics of these films. The composition of films, Ce$_{0.8}$Sm$_{0.2}$O$_{2-\delta}$, is selected in this study because it has been commonly used to produce Sm-doped CeO$_2$ thin films on metal substrates (Li et al., 2008) and (Phok & Bhattacharya, 2006) and demonstrates improved elastic constant, $E$, (Pan et al., 2009) which is beneficial in increasing films’ critical thickness.

2. Experiment

Ce$_{0.8}$Sm$_{0.2}$O$_{2-\delta}$ thin films were produced on Ni-5%W substrates by spray deposition of cerium and samarium nitrate hexahydrate diluted with H$_2$O. Ce(NO$_3$)$_3$ was initially dissolved in ultrapure water and stirred for 30 minutes. Sm(NO$_3$)$_3$ was added to the solution, which was 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 further diluted
with H₂O to achieve a Sm-Ce nitrite concentration of 0.03 M. The molar ratio of Sm and Ce in the solution was 1:4, aiming to achieve Ce₀.₈Sm₀.₂O₂₋δ stoichiometry.

An ultrasonic nebulizer (MY-520 A, GE Sci-Tech, Xinxiang, China) was used to generate aerosol particles deposited on Ni-5%W substrate (5×10 mm). The droplet size distribution at the nebulizer’s discharge point was between 0.5 and 10 μm, with the maximum at around 2.4 μm, as measured by a laser particle counter (Model 4705, Aeronanotech, Moscow, Russia). Before each production run, the substrate was placed on a hot ceramic plate and kept at 150°C –170°C during the entire fabrication procedure. Keeping the substrate at this temperature was crucial to ensure instant evaporation of water from each drop immediately after its collision with the substrate’s surface. The distance between the nozzle and the substrate was 5 mm, and the deposition time varied between 60 and 180 seconds.

Once deposition was complete, the deposited films were 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 and then sintered at 900°C for 3 hours. To prevent oxidation of Ni(W) substrate, samples were placed within a graphite lining to ensure oxygen reduced conditions, as the graphite covers proved to be effective enough in preventing the occurrence of oxidation.

Thin film phases and crystallite parameters were determined by X-ray diffraction (XRD) using copper Kα radiation (λ=1.5406 Å). The surface morphology and microstructure of thin films were characterised using scanning electron microscopy (SEM) with energy dispersive (EDS) X-ray analysis. The valence state of Ce and Sm in thin films and their elemental ratio were investigated by X-ray photoelectron spectroscopy (XPS).
3. Results and discussion

The deposited Ce$_{1-x}$Sm$_x$O$_{2-\delta}$ thin films had a pinhole-free, uniform surface structure. (Fig. 1) shows SEM images of Sm-doped CeO$_2$ thin films produced by 1 minute spray deposition and sintered at 900°C for 3 hours. The films have a smooth surface morphology, consisting of well-packed grains that were 20–100 nm across. The thickness of the crystallised thin film was about 50–160 nm, depending on the deposition time. Further increase of deposition time beyond 3 minutes caused unfavorable cracks. More studies are required to find the optimum film thickness, and also possibly to apply multiple, sequential deposition heat treatment steps.

![SEM images of Sm-doped CeO$_2$ thin films](image)

Fig. 1 : Scanning electron microscope image of Sm-doped CeO$_2$ thin films: (a) near the edge and (b) the surface at higher magnification.
The XRD analysis revealed that the films have a preferred c-axis orientation (Fig. 2), with a dominant (2\,0\,0) peak, compared with precursor powder calcined under the same conditions. This confirms that the preferable orientation of films in <00n> planes following the Ni(W) substrate texture has been achieved. An excessive quantity of graphite near the substrate may result in the deposition of amorphous carbon, as demonstrated in (Fig. 2 b) by two humps in the XRD pattern. A small (1\,1\,1) peak is also observed. Table 1 gives the crystallographic and microstructural characteristics of the films. The calculated lattice constant is 5.41–5.44 Å, which is within the range of reported lattice constants of Sm-doped CeO$_2$ thin films (Phok & Bhattacharya, 2006) and (Patil & Pawar, 2007). The crystallite size of the films, $d$, is 20–24 nm, as calculated by Scherrer’s formula:

$$d = \frac{k\lambda}{b\cos\Theta}$$

Where $k=0.9$ (Patterson, 1939), $\lambda$ is the wavelength of XRD, $\beta$ is a full width at half maxima of the (2\,0\,0) peak, and $\Theta$ is the corresponding Bragg angle. These values are similar to the grain size in Sm-doped CeO$_2$ thin films prepared on Ni by aerosol-assisted MOCVD (Jiang et al., 2006) and slightly lower than the crystalline size of 28 nm in Sm-doped CeO$_2$ thin films on Ni formed by electro-deposition (Phok & Bhattacharya, 2006).
Fig. 2: X-ray diffraction patterns for (a) the precursor powder and (b) Sm-doped CeO$_2$ thin films heat-treated at 900°C in reduced atmosphere.

Table 1: Typical characteristics of spray-deposited Ce$_{1-x}$Sm$_x$O$_{2-δ}$ thin films

<table>
<thead>
<tr>
<th>Sm-doping, $x$</th>
<th>Thickness, nm</th>
<th>Lattice parameter, $a$ (Å)</th>
<th>Crystallite size, nm</th>
<th>Grain size, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15–0.25</td>
<td>50–160</td>
<td>5.41–5.44</td>
<td>19.6–29.9</td>
<td>20–100</td>
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</tbody>
</table>

The XPS spectrum of the films (Fig. 3) indicates the presence of cerium (Ce 3d peaks) and samarium (Sm 3d) on the surface.
Cerium 3d spectra (Fig. 3 b) are composed of two multiplets, corresponding to the spin-orbit split 3d5/2 and 3d5/2 core holes. The profile of these six peaks is typically observed in CeO2 oxides (Holgado, Alvarez & Munuera, 2000), indicating that most of the cerium is in the Ce4+ valence state, despite being sintered under reducing conditions. The Sm/Ce ratio in the films was estimated by comparing Sm 3d and Ce 3d XPS spectra (Fig. 3 a and b). The determined Sm content, x, in Ce1-xSmxO2-δ 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 the EDS spectra. These values correspond well to the molar ratio of Sm:Ce=0.25 in the precursor solution.
Fig. 3: X-ray photoelectron spectrum of sintered Sm-doped CeO$_2$ film
4. Conclusion

Ultrasonic spray deposition was used to fabricate Sm-doped CeO$_2$ thin films on textured Ni-W substrates from metal-organic solutions. The decomposition of nitrite precursor materials and subsequent sintering of oxide films were performed under reducing conditions without introducing hydrogen into the neutral atmosphere. The sintered films exhibit smooth surface morphology and $c$-axis orientation. Our findings confirm that this technique is feasible for the production of high-quality thin films, and looks very promising for the further development of buffer layer formation in textured HTS tape applications.
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