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Microstructural evolution in manganese cobaltite films grown on Crofer 22 APU substrates by pulsed laser deposition

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ABSTRACT

The use of pulsed laser deposition to produce high-quality manganese cobaltite spinel coatings on Crofer 22 APU substrates has been investigated, and the microstructures of the coatings have been studied using a combination of X-ray diffraction and electron microscopy techniques. It is shown that deposition from ceramic $Mn_{1.5}Co_{1.5}O_4$ targets at a chamber pressure of 2.8×10^{-4} mTorr N_2 with the substrate pre-heated to 400 °C resulted in smooth, dense polycrystalline coatings. These coatings contain a mixture of rock-salt (Mn,Co)O and FCC Co phases due to reduction of the target material in the plume during deposition. Post-deposition annealing at atmospheric pressure in laboratory air at 800 °C led to re-oxidation of the coatings to give spinel phases with a thin chromia layer at the interface with the substrate. An annealing time of 0.5 h resulted in a coating with a fine uniform mixture of tetragonal and cubic spinel phases. The presence of pores at the location of the prior Co grains and at the original coating surface was used to infer the mechanisms by which the re-oxidation occurs. An annealing time of 14 h led to phase segregation in the coatings with more Co-rich cubic spinel at the surface and at the coating/substrate interface, and more Mn-rich tetragonal spinel in the center of the coating. There is Cr in the cubic phase only, indicating that the phase segregation occurs due to outward diffusion of Cr from the substrate through the chromia layer. There are local variations in the porosity and surface morphology of the coating, which appear to be correlated with the orientation of the underlying substrate grains. These observations indicate that control of grain structure in the substrate may be necessary to promote microstructural stability in such coatings.

1. Introduction

The development of intermediate temperature (650–800 °C) solid oxide fuel cell (SOFC) stacks raises many interesting material opportunities and challenges. For example, in this temperature range one can use high-temperature metallic alloys to produce the interconnects between individual cells in a stack. These interconnects provide structural stability, direct the fuel and air flows, and transport the electrical current generated at the electrodes. The advantages of metallic alloys for such applications include low cost, good formability and high electrical conductivity, but there are challenges both with the oxidation resistance of the alloys themselves and with the electrical resistivity of most oxide scales that form during service. The interconnect alloys of choice are all chromia-formers, such as Ni-based superalloys and ferritic stainless steels, because Cr_2O_3 scales are semi-conducting [1]. Unfortunately, thick chromia scales can develop on bare alloy surfaces due to the high O_2 partial pressures and the presence of moisture in the cathode environment [2,3]. Such thick chromia scales can lead to unacceptably high ohmic losses between the interconnect and the electrodes [4], and could also result in oxide scale spallation [5]. Moreover, Cr-containing oxides and oxy-hydroxides may volatilize from the chromia scale surface and deposit at active cathode sites causing activation losses [6]. The long-term degradation of SOFCs can be minimized with the use of protective coatings to reduce the chromia scale growth rate [7], spallation [5], and volatilization of Cr species [8]. The first coating materials considered were La-based perovskites doped with alkaline earths [9], transition metals [10], and rare earths [11] due to their established use as electrodes and as ceramic interconnect materials in high-temperature SOFCs. Most reports have shown that such perovskites are unsuccessful as protective coatings due to their high ionic conductivities [12]. Much better performance has been obtained using spinel oxides, and indeed coatings based on such phases have already been implemented into large-scale SOFC systems [13].

The spinel coating composition that has attracted the most attention is $Mn_{1.5}Co_{1.5}O_4$ (MCO) due to its phase stability and high polaronic conductivity [14,15]. Such MCO coatings are often applied via a reactive consolidation process [16,17], which involves: application of a MCO slurry, drying, reduction in moist H_2-based forming gas to form a MnO/Co phase mixture, and then re-oxidation in air to form a relatively dense MCO coating. We have shown previously that such coatings inhibit the oxidation kinetics significantly for Haynes 230 and Crofer

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22 APU under SOFC operating conditions [7], and that Cr-rich spinel reaction layers (RLs) form at the interface with the alloy substrates [18,19]. It may be the transport through this Cr-rich spinel RL that retards chromia scale growth [20], but the presence of this RL may also lower the overall conductivity of the coating [21] and increase the potential for Cr volatilization [22]. The reactive consolidation process results in a complex coating microstructure: the initial dried slurry is highly porous, but densifies significantly during the reduction and re-oxidation process [23]. This process is accompanied by the formation of a Cr_2O_3 scale at the interface and outward diffusion of Cr into the coating to form the spinel RL [7]. Our recent X-ray channeling experiments [24,25] suggest that the strong tendency for Cr to occupy the octahedral sites in the spinel structure may be responsible for some of the unusual microstructural features that form during the development of the spinel RL [18,19].

Here we report a study on the use of pulsed laser deposition (PLD) to produce MCO coatings on Crofer 22 APU substrates. While physical vapor deposition techniques are inherently less scalable than the slurry-based reactive consolidation process, they do offer the possibility of forming more uniform and much denser coatings. Such coatings are of interest as model systems to help study microstructural development in the coating phases, and might be practical for certain small-scale niche SOFC systems. There have been a few previous reports on the use of PLD to grow perovskite films [26,27] and $MnCr_2O_4$ spinel films [27] onto interconnect alloys, but as far as we are aware this is the first reported use of PLD to deposit MCO. We have used a combination of X-ray diffraction (XRD) and electron microscopy techniques to reveal the details of the microstructures both in as-deposited films and in films after post-deposition oxidation heat-treatment. The implications of these observations for the microstructural development in this system are discussed.

2. Experimental method

The PLD was performed using a ceramic $Mn_{1.5}Co_{1.5}O_4$ spinel target, which was 25 mm in diameter and 10 mm in thickness. This target was produced by: synthesizing powders of this composition utilizing the glycine nitrate process [28], cold pressing in a floating die to form a disk-shaped compact, cold isostatic pressing to increase green density, and finally pressure-less sintering to give a final porosity of ≈30%. The details of the process were reported previously [25]. The phase purity of the target was confirmed using Raman spectroscopy and X-ray diffraction (XRD), and no phases other than the tetragonal Mn_2CoO_4 and cubic $MnCo_2O_4$ spinels were detected.

PLD films were deposited onto 200 μm thick, cold-rolled coupons of the alloy Crofer 22 APU (ThyssenKrupp AG, Germany [29]); the composition limits for the alloy are given in Table 1. Preliminary experiments revealed profound orientation effects due to defects and/or crystallographic texture at the substrate surface. Thus, for all of the experiments presented here, the substrate was polished mechanically and then electrolytically in an aqueous mixture of sulfuric and chromic acids at 50 °C. The combined effect of these polishing processes was to remove a surface layer of approximately 50 μm in thickness.

Deposition was performed using a Coherent Inc. Lambda Physik: Compex 201 KrF pulsed eximer laser ($\lambda = 248$ nm). The deposition conditions used were: pulse energy of 190 mJ, laser fluence of 1 J/cm^2, repetition rate of 5 Hz, pulse length of 25 ns, chamber pressure of 2.8×10^{-4} mTorr N_2, target/substrate distance of 80 mm, and a deposition time of 2.5 h. Prior to deposition, the back side of the substrate was heated to 400 °C using a cartridge heater and the temperature was continuously monitored using an attached thermocouple. During deposition the substrate temperature was kept constant, and both the target and substrate were rotated to ensure uniformity of the thickness and composition in the deposits. Some of the deposits were subjected to post-deposition annealing ex situ at 800 °C for 0.5 and 14 h in a tube furnace at atmospheric pressure in laboratory air.

Table 1
Composition specification for Crofer 22 APU. All values are in weight % [29].

	Cr	Fe	C	Mn	Si	Cu	Al	S	P	Ti	La
Min	20.0			0.30						0.03	0.04
Max	24.0	Bal.	0.03	0.80	0.50	0.50	0.50	0.02	0.05	0.20	0.20

The structures of both the as-deposited and the annealed films were characterized using XRD with a Bruker 5005 diffractometer. The XRD spectra were acquired by scanning over the angular range $2\theta = 15°$ to 120° at a scan speed of 25 s/step with a step size of 0.02° using Cu Kα radiation with a monochromator. The morphologies of the films were evaluated by secondary electron (SE) imaging using the electron columns of FEI Strata 400S and Helios Nanolab G3 dual beam FIB instruments. These instruments were also used to perform site-selective sample preparation for transmission electron microscopy (TEM). The procedure used was to deposit protective Pt layers over the region of interest by using first the electron beam and then the Ga^+ ion beam. Trenches were then cut through the deposits and into the underlying substrates, the lamellae between the trenches were then lifted out and mounted onto copper Omni grids. A scanning transmission electron microscopy (STEM) detector and flip-stage were used for final thinning. Ga^+ beam currents were reduced iteratively to a value of 9.7 pA during final milling to avoid excessive Ga^+ implantation and beam damage. The resulting samples were examined in FEI Tecnai T12, JEOL 2010 and FEI Talos F200X TEMs operating at accelerating voltages of 120, 200 and 200 kV, respectively.

3. Results

3.1. As-deposited films

The as-deposited films were firstly analyzed by XRD. Data such as those shown in Fig. 1(a) contain two main sets of peaks: those corresponding to the body-centered cubic (BCC) structure of the ferritic Crofer substrate and a second set from the PLD coating. The relative intensities of the BCC peaks varied from one location to another on the sample because the grain size at the surface of these electropolished substrates (20 μm) is comparable to the collimated X-ray beam diameter used. The peaks from the deposit were not those expected for the spinel structure of MCO, but instead corresponded to a face-centered cubic (FCC) lattice with a lattice parameter, a_0, of 0.4388 nm. This value of a_0 lies between those for CoO (0.4267 nm) and MnO (0.4442 nm), both of which exhibit the rock-salt structure (space group Fm3m). In certain XRD scans, where the Crofer grains were oriented such that the intensity of the 110_{BCC} peak was unusually low, there were small shoulder peaks that were subsequently shown to be from metallic Co as described below. An example of this is shown in the inset to Fig. 1(a).

The surface morphology of the as-deposited film was investigated using SE imaging and a typical image is shown in Fig. 1(b). The contrast in such images was fairly uniform suggesting that the films are relatively smooth, although there were subtle differences in contrast from one region to another. Since energy-dispersive X-ray spectrometry (EDXS) data obtained from such regions showed no differences in chemical composition, it seems likely that these contrast effects correspond to variations in the details of the deposit surface topography from one substrate grain to another.

A montage of BF TEM images obtained from a FIB-cut cross-section through the deposit is shown in Fig. 1(c). Such images confirm that the film is smooth and uniform with a deposit thickness of 680 ± 14 nm. The film exhibits a columnar microstructure throughout most of the thickness, with a mean grain width of 95 ± 37 nm measured parallel to the film/substrate interface. There are more equi-axed dark features in the regions adjacent to the deposit/substrate interface. The mean dimensions of these features measured parallel and perpendicular