The influence of substrate surface treatment on the electrodeposition of (Co,Mn)$_3$O$_4$ spinel precursor coatings

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Abstract

The electrodeposition of (Co,Mn)$_3$O$_4$ spinel precursor layers has emerged as a new method to prepare metallic interconnect coatings for solid oxide fuel cells (SOFCs). (Co,Mn)$_3$O$_4$ spinel films can be obtained via the oxidative heat treatment of an electrodeposited Co-Mn alloy layer. Herein, the effects of sandblasting stainless-steel substrates on the electrodeposition of the Co-Mn alloy were investigated. Sandblasting increased Co content in Co-Mn alloy, decreased the onset time of nucleation, and lead to surface nanocrystallization. Furthermore, sandblasting the substrate prevented the formation of the metal hydroxide interlayer, accelerated interdiffusion, and improved the adhesion of the (Co,Mn)$_3$O$_4$ spinel coatings.

1. Introduction

Electrodeposition is a convenient and effective method of preparing coatings used in many engineering applications [1, 2]. In recent years, (Co,Mn)$_3$O$_4$ spinel coatings have attracted attention as metallic interconnect coatings, for solid oxide fuel cells (SOFCs), because their thermal expansion coefficients match well with ferritic stainless steel and they have high electrical conductivities. An emerging method to prepare (Co,Mn)$_3$O$_4$ spinel coatings is to electrodeposits a Co-Mn alloy on stainless steel and then oxidize the alloy at elevated temperatures [3–6]. The advantages of this method are the low cost and the ability to prepare coatings with complex geometries [7, 8]. Mn has a low reduction/oxidation (redox) potential in aqueous solutions ($\text{E}_{\text{Mn}}^{\text{redox}} = -1.18$ V versus SHE). Thus, it is difficult to electrodeposit Mn alloy from aqueous solutions due to the low current efficiency, i.e., hydrogen evolution is faster than Mn deposition [9–11].

Various additives have been used to improve the quality of the Mn alloy electrodeposition and inhibit hydrogen evolution [3, 4, 12, 13]. Wu et al. used glucose as a complexing agent to prepare a Co-Mn alloy using direct current and pulse electrodeposition methods. Their results showed that the coating deposited by direct current electrodeposition was porous and thin, whereas the coating prepared by pulse electrodeposition had cracks on the surface [3, 4]. Zhang et al. electrodeposited the Co-Mn alloy, with a higher Mn content, by using a chloride system and disodium ethylenediaminetetraacetate (EDTA) as a complexing agent. The resulting alloy had no cracks or pores. EDTA significantly lowers the reduction potential of Co, while only slightly altering Mn, thus reducing the gap in the reduction potential between Co$^{2+}$ and Mn$^{2+}$ [5, 6].

The electrodeposition process is also influenced by several other operating parameters, such as the composition of the plating bath, applied cathodic current density, solution temperature, and pH. All of these process conditions can affect the properties of the coating, such as microstructure, morphology, and chemical composition [14–19]. Sandblasting can be used to not only surface plastic deformation, but it can also increase its surface area [20–22]. Thus, by sandblasting a substrate, for electrodeposition, the electrochemically active area can be substantially increased compared to a flat electrode. Therefore, the effect of substrate sandblasting on the electrodeposition of Co-Mn alloys should be investigated.
In this study, the influence of substrate sandblasting on the surface deformation of an electrode was characterized by transmission electron microscopy (TEM). Also, the electrochemical behavior of the Co-Mn alloy co-deposition was investigated by anodic linear stripping voltammetry (ALSV) and chronoamperometry (CA). Furthermore, the effect of the substrate sandblasting surface treatment on the heat treatment process to oxidize the alloy to (Co,Mn)3O4 spinel was examined. The surface morphology and microstructure of the (Co,Mn)3O4 spinel coatings were characterized by scanning electron microscopy (SEM). This research can contribute to the development of surface protective coatings for metallic interconnects in SOFCs.

2. Material and methods

2.1. Co-Mn electrodeposition and heat treatment

430 s stainless steel was used as the substrate for the electroplating of the Co-Mn alloy. The electrodeposition and oxidative heat treatment have been described previously [5, 6]. All coupons were separated into two groups, one was mechanically polished up to 800# with silicon carbide papers, and the other one was sandblasted using an air-blast machine with Al2O3-SiO2 mixture beads at 0.2 ~ 0.4 MPa [23].

After surface treatment, all coupons were cleaned ultrasonically in distilled water, acetone, and absolute ethanol. The bath used for the electrodeposition of Co-Mn alloy films contained 0.05 M CoCl2, 0.05 M EDTA, 1.25 M MnCl2, 0.56 M NH4Cl, and 0.20 M NH4Br, the pH of the solutions was 4.5. Electrodeposition was carried out, at room temperature under ultrasonic agitation at a frequency of 50 Hz, at a current density of 125 mA cm−2. Heat treatment was conducted by heating for 30 min at 750 °C in an argon environment to remove hydrogen, and then oxidized by heating for 2 h at 800 °C in an atmospheric environment.

2.2. Materials characterization

A JEOL 2100F TEM was used to investigate the surface microstructure of sandblasted 430SS substrates using the bright field (BF) imaging mode. The crystal structure was characterized by selected area electron diffraction (SAED) at an accelerating voltage of 200 kV. A field emission SEM (FEI INSPECT F50) was used to investigate the microstructures of Co-Mn coatings before and after heat treatment, and energy-dispersive x-ray spectroscopy (EDS) was used to analyze the chemical composition of the coatings. Surface roughness of the specimens with grounding and sandblasting treatment was measured by an Olympus LEXT OLS4100 3D Measuring Laser Microscope.

2.3. Electrochemical characterization

Electrochemical characterization was carried out using a PARSTAT 4000 electrochemical workstation using a traditional three-electrode setup. The ALSV and the CA were tested in the same electrodeposition solution detailed above. For ALSV measurements, the potential was maintained at −1.7 V for a period of time, and then the anode scanning was run at a rate of 20 mV s−1. Before each measurement, working electrodes were mechanical polished with alumina or sandblasted according to test requirements [6].

3. Results and discussion

3.1. Characterization of the substrate surface morphology

Figure 1 shows the surface morphology and corresponding surface roughness measurements for the machined and sandblasted specimens. Compared to mechanically ground specimen (figure 1(a)), a large number of random deformation in the form of bulges and pits, can be observed on the surface of the sandblasted specimen (figure 1(b)). From the surface profile roughness measurements as shown in figures 1(a-1)–(a-4) and (b-1)–(b-4), where the assessment length is about 1000 μm for each measurement and the scale of surface profile is μm, it can be seen that the maximum height of surface profile of the mechanically ground specimen is about 1.5 μm while that of the sandblasted specimen is about 20 μm, suggesting the enhanced effect of sandblasting treatment on the surface roughness. Figure 2 shows the bright field image of a deformed region on the sandblasted 430SS. Fine equiaxed grains are observed with a grain size of approximately 50 nm. The corresponding SAED pattern (figure 2) also indicates the fine grains at the nanoscale. This morphology is similar to the surface nanocrystallization caused by severe plastic deformation [24, 25]. Through the surface deformation, a high-density of dislocations are generated, which can rearrange, under stress, to form dislocation networks and lead to the formation of nanocrystallites [26].

3.2. Characterization of the Co-Mn alloy coatings

Figure 3 shows the cross-section morphologies of the electrodeposited Co-Mn alloy coatings on as-received 430SS and sandblasted 430SS substrates. From figure 3(a), it can be seen that the Co-Mn alloy coating was
uniform, dense, and adhered well to the sandblasted substrate. EDS spot analysis indicates that the alloy coating is composed of 77 at% Cr, 22 at% Mn, and 1 at% Fe. Figure 3(b) shows the cross sectional image of the Co-Mn coating deposited on the unsandblasted specimen. EDS spot analysis indicates that the outer layer is composed of 58 at% Co and 42 at% Mn, while the inner layer consists of 24 at% Co, 28 at% Mn, 38 at% Fe and 10 at% Cr. In addition, an interlayer between the coating and the substrate, with the darkest contrast, can be seen in figure 3(b). Based on the above analysis, it can be speculated that the sandblasting process also has a significant influence on the elemental composition of the coating, as detected via EDS. The ratio of the Co to Mn EDS signals was 1.4 for coatings on substrates without sandblasting, and 3.5 for coatings on sandblasted substrates. This result indicated that by sandblasting the substrate, the Mn content in the electroplated alloy coating is decreased. This effect is related to the different rates of the steps during the electodepositing processes.

It has been demonstrated that sandblasting increases the surface area compared to the geometrical area of the flat electrode. Furthermore, it has been reported that the Mn electroplating is mainly controlled by
electrochemical polarization. Thus, the reaction rate decreases when the surface area of the electrode increases. Conversely, Co deposition is mainly controlled by concentration polarization, and its reaction rate is only related to the apparent surface area of the electrode and not to the actual surface area. Therefore, the microscopic surface area of the electrode has less of an effect on the Co deposition than on the Mn deposition. Thus, the Mn content of the electrodeposited alloy coating, on the sandblasted substrate, decreased compared to the allow coating on the untreated substrate.

Also, there is a dark layer in figure 3(b), which is consistent with the presence of a mixture of Mn(OH)\textsubscript{x} and Co(OH)\textsubscript{x}. The metal hydroxide layer has also been observed in Zn-Mn [13], Mn-Cu [14], and pure Mn films [9]. It has been shown that the Co-Mn co-deposition potential is very negative (> −1.7 V) [6]. Therefore, for the electrodeposition of Co-Mn alloy, nucleation and growth are accompanied by electrolyte breakdown. When the negative potential is applied, the pH at the electrode-electrolyte interface increases, leading to the formation of metal hydroxides that compete with metal deposition [27].

3.3. Characterization of the (Co,Mn)\textsubscript{3}O\textsubscript{4} spinel morphology

Figure 4 shows the surface morphologies of Co-Mn coatings deposited on 430SS with and without sandblasting after heat treatment. The (Co,Mn)\textsubscript{3}O\textsubscript{4} spinel coating on the sandblasted substrate is compact, complete, and free of cracks, whereas the coating on 430SS without sandblasting has severe cracking and spalling. Those cracking and spalling observation may be caused by the weak bond strength between the coating and the substrate due to the existence of a metal hydroxide interlayer. During the heat treatment, the following reactions occur: (i) hydrogen is removed from the coating, (ii) the metals are oxidized by the residual oxygen in the furnace, and (iii)
Metal hydroxides are converted to metal oxides via dehydration. The second reaction would cause volume expansion, while the third reaction would cause volume contraction. For the coatings on sandblasted 430SS, oxidation during the heat treatment fills the gaps in the crystallites and makes the coating more compact. For the coatings on 430SS without sandblasting, the hydroxide conversion via dehydration causes volume contraction of the inner layer and reduces the attachment area between the coating and the substrate, thus, causing cracking and spalling.

3.4. Characterization of the electrodeposition process

The nucleation mechanism was analyzed by CA at a constant potential of −1.7 V for 300 s, as shown in figure 5. According to nucleation theory, the nucleation process leads to an increase in the current, and then the current decreases and tends to stabilize during the growth process after nucleation [28, 29]. Figure 5 indicates that the onset of deposition on 430SS without sandblasting—the time to reach a peak in the current—is longer than 30 s. Therefore, the Co-Mn electrodeposition did not occur in the first 30 s. However, when using sandblasted 430SS (curve b in figure 5), the nucleation time is reduced to approximately 5 s.

To further analyze the nucleation time of the Co-Mn alloy, ALSV was performed at −1.7 V for 30 s and 100 s with and without sandblasting; the results are shown in figure 6. The first peak (Ia1), at lower potentials, is related to anodic Mn dissolution. The second peak (Ia2), at higher potentials, is related to anodic Co dissolution [6].

For the substrate that was not sandblasted, the Mn dissolution peak (Ia1) did not appear within 30 s, which means that the Co-Mn co-deposition did not occur (curve 6a). However, when the deposition time was extended to 100 s, the Mn Ia1 peak appears (curve 6b), which means that Co and Mn are co-deposited. These results indicate that more than 30 s are needed for the onset of nucleation to co-deposit Co and Mn at −1.7 V without sandblasting. Interestingly, after sandblasting, both the Ia1 peak and the Ia2 peak appear (curve 6c) within the 30 s deposition at −1.7 V. This result indicates that Co and Mn have been co-deposited. Co-deposition can occur before 30 s because the onset of nucleation is 5 s on sandblasted substrates (figure 5(b)). This change indicated that sandblasting could contribute to crystal nucleation, and promote co-deposition of Co and Mn. Also, there is another peak IIa in curve c, which is related to reaction (i), which has been previously described [6], where H4L is used to represent EDTA.

\[
\text{Mn} + 2\text{OH}^- + \text{H}_2\text{L}^{2-} + \text{Co}^{2+} = \text{CoL}^{2-} + \text{Mn}^{2+} + 2\text{H}_2\text{O} + 2\text{e}^- \\
\text{(1)}
\]

3.5. Effect of sandblasting on the nucleation process

The electrodeposition of metals from aqueous solutions is a heterogeneous process involving various stages, including the transport of solvated species from the bulk solution to the electrode surface, followed by their reduction at the electrode-solution interface with the formation of nuclei. Further growth of the nuclei may occur on the surface of the substrate, leading to the formation of metallic deposits [30]. The rate of the electrocrystallization process may be limited by mass transfer or by the formation of nuclei. In this work, the concentration of Mn\(^{2+}\) was 1.25 M, so the mass transfer of Mn\(^{2+}\) is not likely the limiting step in the co-
deposition of the Co-Mn alloy. Therefore, the formation of nuclei is likely the limiting step, leading to the inability to co-deposit Co and Mn at \(-1.7\) V for 30 s, without sandblasting.

Sandblasted surfaces contain many bulges, pits, and grain boundaries that possess lattice defects. The surface energy of defects is relatively low; therefore, it is easier to overcome the energy barriers to nucleation. The number of nucleation active sites increases because there are many defects after sandblasting \([20, 31]\).

Conversely, when the electrodeposition surface was relatively smooth and regular, it presents significantly less active sites for nucleation, primarily grain boundaries. Thus, the nucleation for the Co-Mn alloy is easier after the substrate surface has been sandblasted. The sandblast treatment reduces the nucleation time from >30 s to \(\sim 5\) s. The formation of metal hydroxides competes with metallic deposition, therefore, with sandblasting the substrate, the formation of metal hydroxide interlayers between the coating and the substrate was inhibited \([27]\).

Figure 7 shows representative SEM micrographs of the Co-Mn coating at \(-1.7\) V for different deposition times. For the sample without sandblasting, no nuclei growth was observed after 30 s (figure 7(a)), many metallic nuclei and metal hydroxides appear after 100 s (figure 7(b)), and a layer of metal hydroxides and metals were observed after 300 s (figure 7(c)). After sandblasting, small nuclei at the defects on bulges are formed after 30 s (figure 7(d)), a thin Co-Mn alloy layer appeared after 100 s (figure 7(e)), and a thickening of the alloy coating is observed after 300 s (figure 7(f)).

To explain the nucleation mechanism, a theoretical model is proposed to describe the effect of sandblasting the substrate on the nucleation and growth processes of the electrodeposition the Co-Mn alloy, which is shown in figure 8. The above results reliably show that sandblasting can improve nucleation and reduce the onset time. Nucleation initially occurs at the active sites on the bulges, and nuclei are later formed at the active sites on the pits, as shown in figure 8. The appearance of the three discharge peaks caused by nucleation in figure 5 (Curve b) also support this theoretical model.

### 3.6. Effect of sandblasting on the adhesion of the \((\text{Co,Mn})_3\text{O}_4\) spinel coating

Figures 1 and 2 show that sandblasting can induce surface nanocrystallization. During high-temperature oxidation, the presence of nanocrystals can accelerate the interdiffusion between the coating and substrate and improve the adhesion of Co-Mn alloy coating. Elemental diffusion between the coating and substrate is accelerated due to the high diffusivity at the grain boundaries (GB) during the heat treatment process. The effective diffusivity \(D_{\text{eff}}\) is a summation of lattice diffusivity \(D_L\) and GB diffusivity \(D_{\text{GB}}\), and can be calculated by the equation:

\[
D_{\text{eff}} = (1 - f)D_L + fD_{\text{GB}}
\]

where \(f\) is the GB area fraction and equal \(2\delta/d\) (\(\delta\) is the GB width and \(d\) the grain size), for metals with a simple cubic lattice structure \([32]\). From equation (1), it is evident that \(D_{\text{eff}}\) would be dramatically increased when the grain size is decreased from 50 \(\mu\)m to 50 nm \([33]\). Therefore, the interdiffusion between the Co-Mn coating and the sandblasted 430SS substrate would be promoted significantly during the heat treatment. The interdiffusion
Figure 7. SEM of coatings obtained in a 1.25 M MnCl₂·4H₂O + 0.05 M CoCl₂·6H₂O + 0.05 M EDTA₂⁻ + 30 g l⁻¹ NH₄Cl + 20 g l⁻¹ NH₄Br solution at −1.7 V for different time with and without sandblasting. (a) 30 s (b) 100 s (c) 300 s (d) 30 s under sandblasting (e) 100 s under sandblasting (f) 300 s under sandblasting.

Figure 8. The nucleation mechanism of sandblasting effect.
layer creates chemical bonding between the coating and the substrate, drastically improving the adhesion of the coating.

Also, sandblasting can improve coating adhesion by a pinning effect. There are many bulges and depressions on the surface of the substrate after sandblasting. These features are engaged with the coating, which plays a role in pinning.

4. Conclusions

In this study, the effects of surface treatment of the substrate on the electrodeposition of a Co–Mn alloy were examined. Based on the above results and discussion, the following conclusions can be made:

(1) Surface nanocrystallization of the substrate was induced via sandblasting, which helped prevent the spalling of the coating after heat treatment. The bond strength between the (Co,Mn)\textsubscript{3}O\textsubscript{4} spinel coating and the substrate was improved by interdiffusion and a pinning effect.

(2) During the electrodeposition of the Co–Mn alloy, the deposition rate of the Co complex ion was mainly related to the apparent surface area of the electrode, while the deposition of Mn\textsuperscript{2+} was mainly related to the real surface area of the electrode. The substrate sandblasting process increased the microscopic surface area of the sample and led to a lower Mn content in the coating.

(3) Sandblasting decreased the onset time of nucleation and effectively prevented the formation of the metal hydroxide interlayer on the Co–Mn alloy coating.

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