



Short communication

Cyclic oxidation of Mn–Co spinel coated SUS 430 alloy in the cathodic atmosphere of solid oxide fuel cells

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ABSTRACT

In order to improve oxidation resistance and long-term stability of the metallic interconnects and prevent the cathode of solid oxide fuel cells (SOFCs) from Cr-poisoning, an effective, relatively dense and well adherent Mn–Co spinel protection coating with a nominal composition of MnCo_2O_4 is applied onto the surfaces of the SUS 430 ferritic stainless steel by a cost-effective sol–gel process. The long-term thermally cyclic oxidation kinetics and oxide scale structures as well as the composition of the coated SUS 430 alloy are investigated. The Mn–Co spinel protection layer demonstrates an excellent structural and thermomechanical stability, and effectively acts as a mass barrier to the outward diffusion of cations, especially Cr, and a lowered parabolic rate constant of $k_p = 1.951 \times 10^{-15} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ is obtained.

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1. Introduction

The interconnect is a key component of the planar solid oxide fuel cell (SOFC) stack that physically separates the oxidant and fuel gases, distributes the gases to electrodes and provides electrical connections between single cells. Because of the relatively high operating temperature, requirements for the interconnect materials are quite stringent, such as high temperature oxidation resistance in both anodic and cathodic atmospheres, high electrical conductivity and thermal expansion compatibility with cell components. The lowered operating temperature of SOFCs to below 850 °C makes it possible to use metallic alloys as the interconnect materials with advantages of easy fabrication, low material cost, high electric and thermal conductivities and structure integrity. Among metallic alloys, Cr_2O_3 -forming ferritic stainless steels are one type of the most promising interconnect material candidates [1–6].

Nevertheless, the Cr_2O_3 -forming alloys are facing challenges that impede their long-term applications in the SOFCs, for instance, insufficient oxidation resistance and the cathode Cr-poisoning [7–9]. The double-layer oxide scale structure ((Mn, Cr)₃O₄ spinel on top of Cr_2O_3) formed on ferritic stainless steels, typically SUS 430 and Crofer22 APU, may offer some improvements in terms of

the Cr-poisoning due to the lower volatility of Cr in the spinel than in Cr_2O_3 [10–13]. However, Cr volatility from the Mn–Cr spinel as well as the exposed Cr_2O_3 may still result in an unacceptable degradation in cell performance, particularly during the early stage of oxidation. In order to overcome the difficulties of insufficient oxidation resistance and Cr-poisoning, various surface coatings have been proposed and investigated, which are relatively dense, electronically conductive, less volatile and chemically compatible with adjacent cell components. Perovskites (La, Sr)MO₃ (M: Mn, Cr or Co) [14–17], Y and/or Co oxides [18–20], (Mn, Cr)₃O₄ and (Mn, Co)₃O₄ spinels [21–24] are proved to be effective on slowing down oxidation kinetics and improving electrical properties, and coatings that contain no Cr are preferred for alleviating the cathode poisoning.

In this paper, a relatively dense Mn–Co spinel coating is developed on the surface of the SUS 430 stainless steel by a cost-effective sol–gel process that is readily applicable to metallic interconnects with various shapes and configurations. The oxidation kinetics and the oxide scale of the coated SUS 430 were characterized and reported in comparison with the uncoated.

2. Experimental

A commercial 1 mm thick SUS 430 stainless steel, provided by Yuhang Stainless Steels Ltd., containing 81.15 wt% Fe, 16.68 wt% Cr, 0.63 wt% Mn, 0.69 wt% Si, 0.08 wt% C and trace amount of Ni, Al, P and S, was selected for this study. Coupons with a

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dimension of 25 mm × 25 mm × 1 mm were obtained by using an electric discharge machine and ground on both sides up to 1200 grits. The ground coupons were ultrasonically cleaned in acetone and ethanol for 15 min, respectively, and dried prior to coating.

The sol-gel solution for obtaining Mn-Co spinel (nominal MnCo_2O_4) coating was prepared by using proportional amounts of manganese chloride tetrahydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$), cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), citric acid monohydrate and ethylene glycol. Dip coating was conducted to coat the solution on the surfaces of the samples. Being dried in an oven, the coated samples were heat treated in an atmosphere of 5% H_2 + 95% N_2 at 750 °C for 1 h and then in air at the same temperature for another 1 h to form Mn-Co spinel coating on the coupon surfaces. The purpose of heat treating the dried coating in reducing atmosphere is to alleviate substrate oxidation during ceramic coating formation and enhance the adherence.

The Mn-Co spinel coated samples were subjected to isothermal cyclic oxidation in a furnace at 750 °C in air for up to 850 h. The samples were taken out from the furnace periodically with a time interval of 50 h, and then weighted using a Sartorius BS 124S electronic balance (accuracy 10^{-4} g) prior to resuming oxidation. Powder Mn-Co spinel materials were also obtained from the sol-gel solution by calcining the dried gel in air at 750 °C for 1 h. A PANalytical X'Pert PRO X-ray diffractometer (XRD) with $\text{Cu K}\alpha$ radiation was employed to analyze the synthesized spinel powder and the oxide scale. The cross-section and/or surface morphology of the as coated and oxidized samples were characterized by a Quanta 200 environment scanning electron microscope (ESEM) with energy dissipation spectroscopy (EDS) attachment.

3. Result and discussion

Fig. 1 shows the XRD pattern of the calcined Mn-Co spinel powder. A single phase of MnCo_2O_4 was identified according to the JCPDS file 84-0482 [25] by diffraction peak position match, confirming the formation of MnCo_2O_4 from the prepared solution and suggesting the possibility to form Mn-Co spinel coating on the SUS 430 stainless steel. Fig. 2 demonstrates the cross-section morphology and the EDS line scan of the as coated SUS 430 alloy. A homogeneous and compact oxide layer, approximately 2–3 μm thick, was formed on the substrate. The EDS line scan shows that elements Cr, Mn, Co and Fe were presented in the oxide scales, with

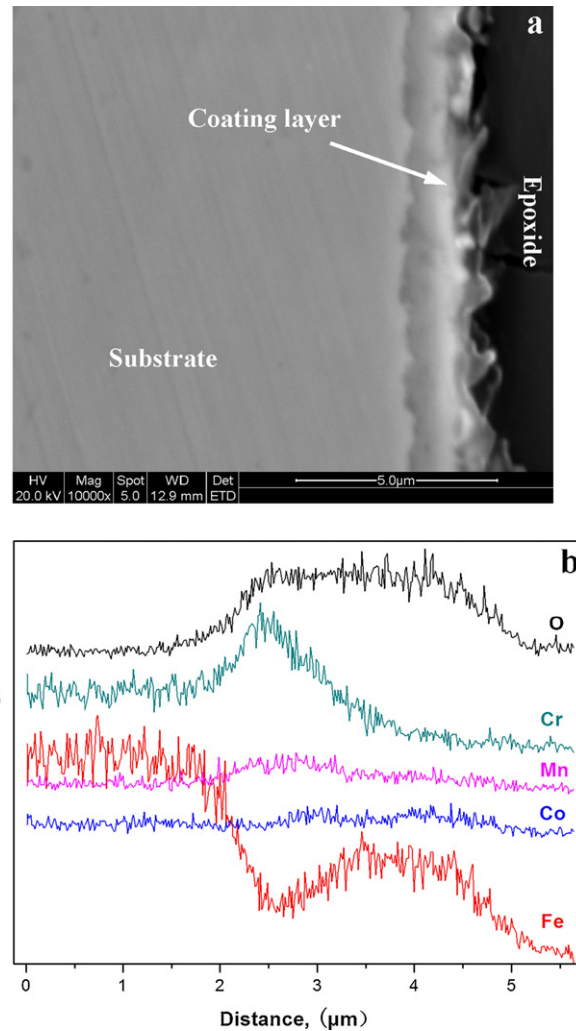


Fig. 2. Cross-section morphology (a) and EDS line scan (b) of the as coated SUS 430 alloy.

rich Cr closing to the substrate, rich Fe on top of the scale and Mn and Co virtually distributed uniformly across the scale. Fig. 3 is the thin film XRD (incident angle 1.2°) pattern of the as-coated SUS 430 sample, Fe_2O_3 and spinel structures were detected. Since the

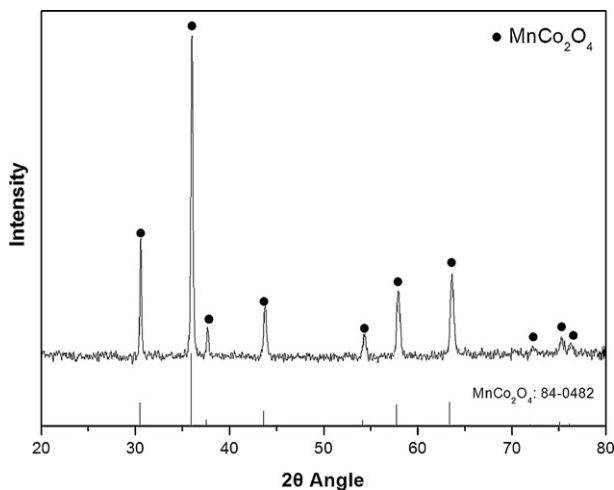


Fig. 1. XRD pattern of the Mn-Co spinel powder from the prepared solution.

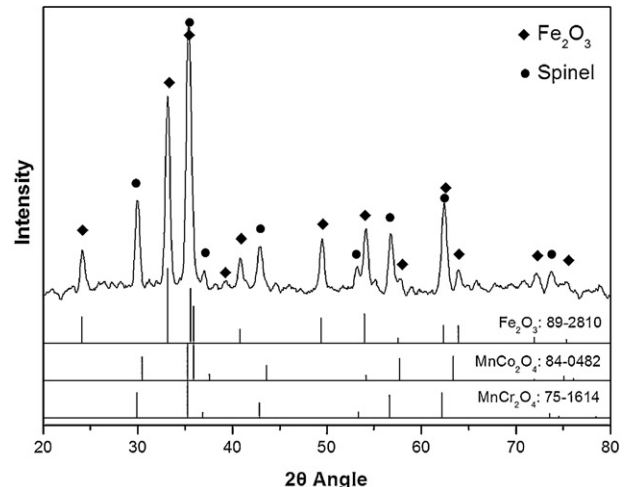


Fig. 3. Thin film XRD pattern of the as coated SUS 430 alloy.

thin film XRD technique was employed, the Cr-rich oxide close to the substrate, usually Cr_2O_3 , was not detected due to the limitation of X-ray penetration depth. The detected spinel structure seems to match MnCr_2O_4 better than MnCo_2O_4 ; however, considering the composition analysis from the EDS line scan and the XRD pattern together, the presence of MnCr_2O_4 may be excluded since no significant Cr was detected in the out layer of the oxide where Fe signal was strong. As known, Fe containing in MnCo_2O_4 increases the lattice parameters of MnCo_2O_4 , resulting in X-ray diffraction pattern shift towards the small angle side; therefore, it can be convinced that the spinel phase formed here is MnCo_2O_4 with partial Fe substitution for Mn or Co.

Fig. 4 shows the surface morphology of the coated SUS 430 alloy that was cyclically oxidized at 750°C in air for up to 850 h (Fig. 4a), in comparison with that of the uncoated SUS 430 alloy oxidized under the same condition (Fig. 4b). The oxidized surface of the coated is homogeneous, relatively dense and smooth, and no spallation is observed. In contrast, that of the uncoated is loosely packed with flaky Cr_2O_3 and prism-shaped MnCr_2O_4 . The cross-section morphology and corresponding EDS line scan

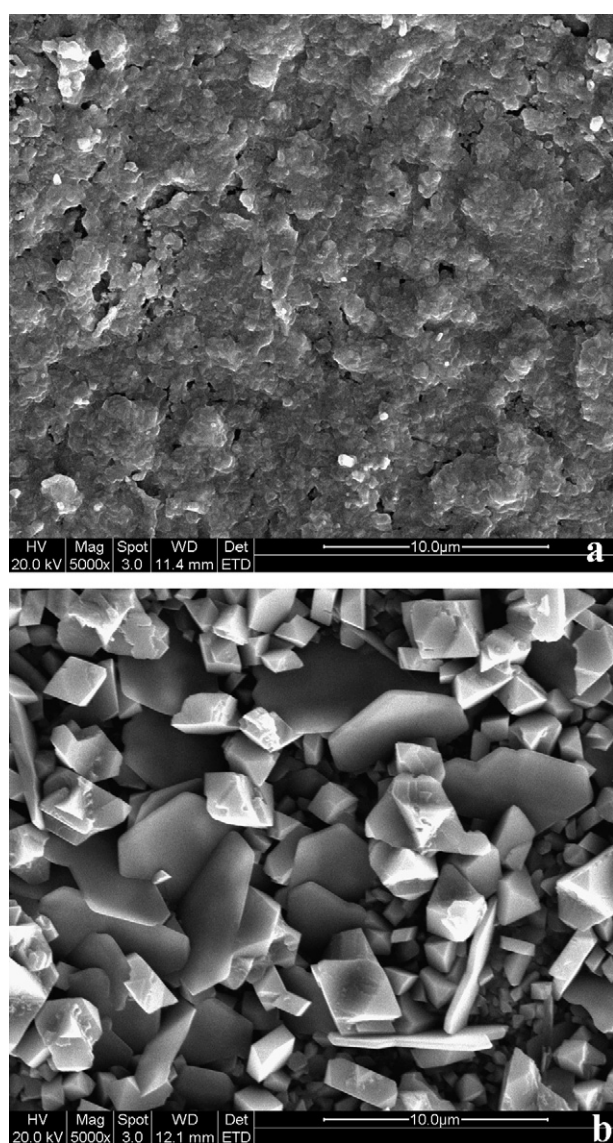


Fig. 4. Surface morphology of the coated (a) and the uncoated (b) SUS 430 alloy oxidized at 750°C in air for up to 850 h.

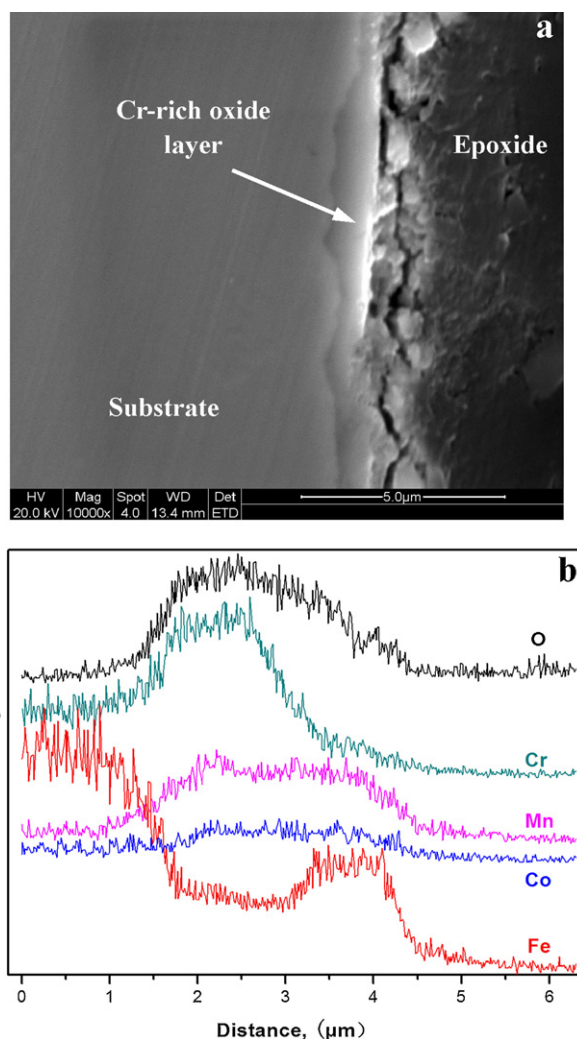


Fig. 5. Cross-section morphology (a) and EDS line scan (b) of the coated SUS 430 alloy oxidized at 750°C in air for up to 850 h.

of the coated SUS 430 alloy cyclically oxidized at 750°C in air for up to 850 h are shown in Fig. 5. Comparing with Fig. 2, no significant difference is observed, the scale is still consisting of a Cr-rich sublayer (Cr_2O_3) and a Fe-rich top layer together with Mn and Co uniformly distributed across the scale. Accordingly, as shown in Fig. 6, the thin film XRD pattern once again confirmed the presence of Fe_2O_3 and Fe-doped MnCo_2O_4 structures with certain amount of Mn_2O_3 formed by continuous outward diffusion of Mn during oxidation. Based on the above results, it can be concluded that the formed coating via sol-gel process is relatively dense and thermally stable in oxidizing atmosphere, and effective on suppressing the outward diffusion of Cr with Fe-doped MnCo_2O_4 located on the top layer of the oxide scale, which is expected to significantly reduce the oxidation kinetics and alleviate the cathode Cr-poisoning.

Fe_2O_3 was rarely observed in the oxide scale of non-coated Fe-Cr alloy in previous studies [3–6,10,11] where a dense sublayer of Cr_2O_3 and a loose MnCr_2O_4 layer were formed. The local oxygen partial pressure balanced by Cr_2O_3 or MnCr_2O_4 was too low to oxidize Fe. Coating application may change the surface oxygen partial pressure during coating formation, which may be favoring the formation of Fe_2O_3 .

Fig. 7 shows the weight gain of the coated SUS 430 alloy sample as a function of oxidation time at 750°C in air for up to 850 h,

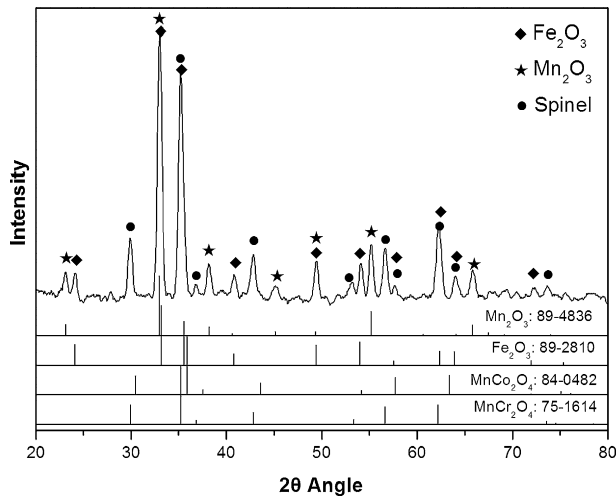


Fig. 6. Thin film XRD pattern of the coated SUS 430 alloy oxidized at 750 °C in air for up to 850 h.

along with that of the uncoated one [10] for comparison. 17 thermal cycles were conducted in between room temperature and 750 °C. In both the cases, the square of the weight gain increases linearly with the isothermal oxidation time, satisfying the parabolic kinetics law described by

$$\left(\frac{\Delta W}{A}\right)^2 = k_p t \quad (1)$$

where ΔW is the weight gain, A is the sample surface area and t is the oxidation time. The slope of the straight line represents the parabolic rate constant k_p in terms of the weight change. The parabolic rate constant is an intrinsic property of an oxidation-resistant alloy and typically used to measure its oxidation resistance. The experimentally obtained k_p of the MnCo_2O_4 coated SUS 430 alloy is $1.951 \times 10^{-15} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$, which is 1–2 orders of magnitude lower than that of the uncoated one ($k_{p,1} = 4.031 \times 10^{-14} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ between 0 and 200 h and $k_{p,2} = 1.54 \times 10^{-13} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ between 200 and 500 h [10]). The oxidation rate is remarkably reduced by the Mn–Co spinel protection coating, which is consistent with the expectation according to the oxide scale characterization.

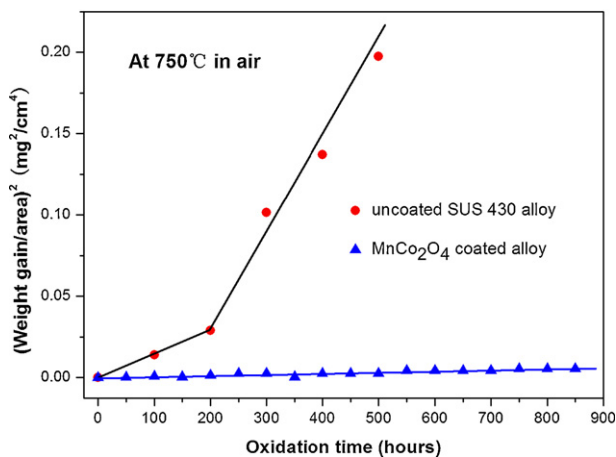


Fig. 7. Weight gain as a function of cyclic oxidation time for the coated and the uncoated SUS 430 alloy at 750 °C in air.

4. Conclusions

The Mn–Co spinel coating was applied to the surface of the SUS 430 stainless steel by the sol–gel process, and the coated alloy was cyclically oxidized in air at 750 °C for up to 850 h. The oxide scales of the as coated and oxidized samples were characterized and cyclic oxidation kinetics of the coated was obtained. The following conclusions can be made from this study:

- (1) The sol–gel process is an appropriate choice to form protection coatings on the surface of SOFC metallic interconnects. Fe-doped MnCo_2O_4 spinel coating can be formed onto the surface of the SUS 430 stainless steels via the sol–gel process, which is thermally and chemically stable during long term cyclic oxidation in between room temperature and 750 °C for up to 850 h.
- (2) The presence of Fe-doped MnCo_2O_4 coating can effectively prevent the Cr-rich oxide (Cr_2O_3) subscale from exposure to air, and in turn, the evaporation of volatile Cr-containing species. As a consequence, suppression of the cathode Cr-poisoning caused by evaporation and condensation of volatile Cr-containing species is expected.
- (3) As protection coating of oxidation, MnCo_2O_4 is adequate to lower the cyclic oxidation rate of the SUS 430 by 1–2 orders of magnitude, a parabolic rate constant $k_p = 1.951 \times 10^{-15} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ can be obtained.

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