



Oxidation behaviour and electrical properties of cobalt/cerium oxide composite coatings for solid oxide fuel cell interconnects



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HIGHLIGHTS

- Co/CeO₂ composites were deposited on two ferritic steels by electrodeposition.
- The Co/CeO₂ coatings reduced the oxidation rates of the steels.
- A low area specific resistance was measured for Crofer 22 APU.
- Crofer 22H had a faster ASR increase than Crofer 22 APU.
- SiO₂ was observed in the metal/oxide interface for Crofer 22H.

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ABSTRACT

This work evaluates the performance of cobalt/cerium oxide (Co/CeO₂) composite coatings and pure Co coatings to be used for solid oxide fuel cell (SOFC) interconnects. The coatings are electroplated on the ferritic stainless steels Crofer 22 APU and Crofer 22H. Coated and uncoated samples are exposed in air at 800 °C for 3000 h and oxidation rates are measured and oxide scale microstructures are investigated. Area-specific resistances (ASR) in air at 850 °C of coated and uncoated samples are also measured.

A dual layered oxide scale formed on all coated samples. The outer layer consisted of Co, Mn, Fe and Cr oxide and the inner layer consisted of Cr oxide. The CeO₂ was present as discrete particles in the outer oxide layer after exposure. The Cr oxide layer thicknesses and oxidations rates were significantly reduced for Co/CeO₂ coated samples compared to for Co coated and uncoated samples.

The ASR of all Crofer 22H samples increased significantly faster than of Crofer 22 APU samples which was likely due to the presence of SiO₂ in the oxide/metal interface of Crofer 22H.

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1. Introduction

Interconnects in solid oxide fuel cell (SOFC) stacks are commonly made of ferritic stainless steel [1]. It is a promising interconnect material because it has a low cost, good formability, high electrical and thermal conductivity and low ionic conductivity [1,2]. Ferritic stainless steels rely on the formation of an outer chromium oxide (Cr₂O₃) scale to protect it against further attack in the highly corrosive SOFC environment [2]. It is currently not possible to use water vapour containing cathode air and ferritic stainless steels without surface modification due to two issues. (I)

At the high operating temperatures of the SOFC stack, chromium can be oxidized to volatile Cr⁺⁶ species, e.g. CrO₂(OH)₂. These volatile species can deposit in the cathode where they cause degradation, a phenomenon known as chromium poisoning [3,4]. (II) The electrical losses in the systems increase unacceptably fast because oxide scales with a poor electrical conductivity form on the interconnect [2,3,5–8].

Coatings have been extensively studied to solve these issues and many good results have been obtained [9]. Cobalt coatings [10,11] and Co/Mn spinel oxide coatings have been shown to very effectively reduce outward chromium migration, which results in a large reduction of chromium evaporation [12,13]. Spinel oxides are oxide materials with the general composition AB₂O₄, where A and B are divalent and trivalent metal ions, respectively [14]. A Co/Mn spinel coating might also provide some resistance against high temperature oxidation of the interconnect [15] but it is desirable to apply a

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more effective coating in order to extend the life time of the SOFC system. During exposure of the interconnect in the SOFC stack, a Cr_2O_3 layer grows underneath a coating due to high temperature oxidation and cause an increase in area specific resistance (ASR). In order to improve a cobalt-based spinel coating against high temperature oxidation, it can be combined with reactive elements, e.g. Ce, Y, La and Hf [16]. Reactive element and their oxides can greatly reduce the oxidation rate and improve the spallation resistance of an alloy [16–19]. This is commonly known as the reactive element effect and reactive elements have been shown effective when added as metallic alloying elements, oxide dispersions [20], in the surface with ion implanting [21] or on the surface as oxides [22]. Cerium is a commonly used reactive element. It has been shown that surface applied CeO_2 significantly decrease the oxidation rate of pure chromium metal [23] of 22 wt. % Cr steel in air at 800 °C [24] and that surface applied CeO_2 can increase the performance of SOFC interconnects [16,24–28].

A CeO_2 coating can reduce the oxidation rate of chromia forming steel but it cannot be used as the only coating material because it is not effective against chromium evaporation as results of the layers being porous and often thin [24,25], due to the high electrical resistance of thick layers. A promising coating strategy is to combine Co-based spinels with CeO_2 in a single coating in order to reduce both the chromium diffusion to the surface of the interconnect and the rate of alloy oxidation. This strategy has been shown successful for a 650 nm Co/Ce coating on Sanergy HT, a steel with 22 wt. % Cr [26].

Spinel can be deposited on ferritic stainless steel by a wide variety of techniques, which are thoroughly reviewed in Ref. [9]. Electroplating is considered to be a very promising process technology for coating deposition because it is a cost effective method that can deposit a uniform, well adherent coating on a complicated geometry [9]. With electroplating, the coating is deposited as a metal and subsequently converted to a spinel by air annealing/oxidation. A limitation of the process is that it is not possible to electroplate metallic coatings of reactive elements from an aqueous electrolyte, due to their low reduction potentials. As an alternative process for depositing a composite coating, reactive elements oxide particles can be codeposited together with a metal. It has been shown that an electrodeposited Ni/ CeO_2 composite coating can reduce the high temperature oxidation rate of a Cr_2O_3 forming steel [29].

In this work, Co/ CeO_2 composite coatings were electrodeposited on steels of the types Crofer 22 APU and Crofer 22H. The coatings were manufactured by codeposition of CeO_2 particles in electrolytically deposited cobalt.

The oxidation properties were assessed by exposing uncoated, Co-coated, and Co/ CeO_2 coated samples of Crofer 22H and Crofer 22 APU in air at 800 °C. The area specific resistances of uncoated samples, Co coated samples and Co/ CeO_2 coated samples were measured in air at 850 °C.

2. Experimental

The steels Crofer 22H and Crofer 22 APU from ThyssenKrupp VDM (nominal compositions are shown in Table 1) were electroplated with Co/ CeO_2 composite coatings and pure Co coatings.

Both steels are high chromium steels specifically developed for SOFC operation and have a Cr concentration of approx. 22 wt. %. The main compositional differences are that Crofer 22H contains W, Nb and has a higher Si concentration. A low Si concentration is important in order to avoid formation of an electrically insulating SiO_2 layer during high temperature exposure of the steel. Crofer 22 APU has been processed using vacuum technology in order to reduce its Si concentration to a very low level. Crofer 22H has a lower cost because it has been processed with conventional technology but consequently has a much higher Si concentration. However, it has been reported that it may be useable as an interconnect material because its content of Nb and W induce the precipitation of Laves phases. Laves phases are intermetallic phases with the composition $(\text{Fe}, \text{Cr})_2(\text{Nb}, \text{W})$ in Crofer 22H [30]. Laves phases increase the creep strength of the steel but equally important, they have a high solubility for Si [30,31]. Because Si is preferentially located in this phase, a semi continuous instead of a continuous SiO_2 layer forms during oxidation [32,33].

The coating deposition method was codeposition of CeO_2 particles in electrodeposited cobalt. The CeO_2 particles was commercially available powder obtained from Nanostructured & Amorphous Materials, Inc., USA and had the nominal size specification 15–30 nm.

The samples measured $20 \times 30 \times 0.3 \text{ mm}^3$. In the upper part of a sample was a 6 mm hole, which enabled them to hang on alumina rods during oxidation tests.

Electroplating was done in Co Watts electrolytes with composition and operating conditions given in Table 2. The sample (cathode) was placed symmetrically between 2 vertically positioned anodes of pure Co. The CeO_2 particles were dispersed in the electrolyte by an overhead propeller of stainless steel during electroplating. The electrolytes had a volume of 8 l and were contained in polypropylene boxes.

The samples were electroplated in a holder that allowed 12 samples separated 1 mm to be electroplated simultaneously. In order to ensure uniform current density and coating thickness on all samples, an outer frame with a width of 23 mm was present around the 12 samples. The frame prevented a thicker deposit on sample edges and corners where the current density – and consequently the deposit thickness – is higher during electroplating.

Pretreatment before electroplating consisted of anodic electrocleaning in an alkaline electrolyte followed by activation in an acidic electrolyte containing NaHSO_4 and Na_2F_2 . The samples were then electroplated with a thin strike layer of Co in an electrolyte

Table 2

Composition and operating conditions of the Co Watts electrolyte and the Co/ CeO_2 Watts electrolyte.

Cobalt sulphate heptahydrate, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	440 g/L
Cobalt chloride hexahydrate, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	35 g/L
Boric acid, H_3BO_3	40 g/L
Cerium oxide, CeO_2 (nano particles 15–30 nm)	0 or 40 g/L
pH	4.3–4.8
Temperature	60 °C
Current density	1.5 A/dm ²
Anodes	Pure cobalt

Table 1

Nominal compositions of Crofer 22 APU and Crofer 22H [54,55].

	Cr	Fe	C	Mn	Si	Cu	Al	S	P	Ti	La	Ni	N	Nb	W
Crofer 22 APU	20.0–24.0	Bal.	<0.03	0.03–0.80	<0.50	<0.5	<0.50	<0.020	<0.050	0.03–0.20	0.04–0.20	–	–	–	–
Crofer 22 H	20.0–24.0	Bal.	<0.03	<0.8	0.1–0.6	<0.5	<0.1	<0.06	<0.05	0.02–0.2	0.04–0.2	<0.050	<0.03	0.20–1.00	1.0–3.0

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