Effect of Co deposition on oxidation behavior and electrical properties of ferritic steel for solid oxide fuel cell interconnects

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ABSTRACT

In this work, a Co layer deposited on DIN 50049 steel by means of pulsed laser deposition was applied for the protection of solid oxide fuel cell (SOFC) interconnects operating on the cathode side. The coated and uncoated steel samples were oxidized in air at 1073 K for 500 h, and their microstructures as well as electrical resistances were evaluated using X-ray diffraction, atomic force microscopy, scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy, and the 2-probe 4-point direct current method. It was demonstrated that the Co coating had reduced the oxidation rate of the steel by nearly a half. The area-specific resistance value of the coated steel was 5×10^{-6} $\Omega \cdot m^2$, which was significantly lower than that of bare steel after 350 h of oxidation at 1073 K. Cr vaporization tests showed that the Co coating was efficient at blocking the outward diffusion of Cr. The obtained results prove that steel coated with a thin film of cobalt was suitable for use as metallic interconnect material in SOFCs operating at intermediate temperatures.

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1. Introduction

Ceramic fuel cells are an environmentally friendly device used to generate electrical energy and heat from oxidation reactions involving gaseous fuels, with an efficiency of up to 80%, obtained by skipping the intermediate step of conversion to thermal and mechanical energy. Currently, intermediate-temperature solid oxide fuel cell (IT-SOFC) stacks capable of high-efficiency operation at lower temperatures (873–1073 K) are the subject of intensive research [1]. The construction of planar-type IT-SOFCs requires bipolar interconnects that feature an electrical conductive path, high mechanical strength, and the separation of the fuel and air supply to the respective electrodes [1,2]. Reducing IT-SOFC operating temperatures makes it possible to employ cost-effective ferritic stainless steel interconnects due to their high-temperature corrosion resistance, which is related to the growth of a protective chromia scale and the compatibility of their thermal behavior with that of solid electrolytes of doped-ZrO$_2$ [3]. However, the excessive growth of chromia and chromium evaporation on the cathode side of the fuel cell may lead to the loss of the protective properties of the scale and the poisoning of cathode material; this subsequently increases both the cell resistance and the polarization resistance [2,4–6].

One possible solution to these problems is to use a commercially available ferritic stainless steel with >20 wt.% chromium content – a

material that is both easy to process and cheap – and to modify it with a protective coating. Some inorganic materials, including La-based perovskites [7,8] as well as Mn-based and Co-based spinels [9–14], may be applied as protective and conducting coatings. Perovskites are widely used as protective-conducting coatings due to their relatively high chemical stability under an oxygen partial pressure gradient, thermal expansion match and high electronic conductivity at operating temperatures ranging from 873 to 1073 K [15–17]. However, these coatings are not effective at limiting the growth of chromia between the coating/substrate interface, due to possible inward diffusion of oxygen via oxygen vacancies in perovskite [18]. Various studies have recently investigated cobalt-based spinel as a promising coating for SOFC applications due to its ability to prevent chromium migration from the chromium-containing steel substrate, and hence the negative consequences related to the emission of volatile Cr-compounds to the cathode side of the IT-SOFC [9–14,19–21]. Pure cobalt oxide, Co$_3$O$_4$, exhibits high electronic conductivity, and it can be further improved by adding manganese, iron, copper, or a combination of these elements [20]. Spinel coatings can also be fabricated in situ by applying a single metal which undergoes oxidation when the IT-SOFC system is put into service. In this regard, the application of coatings utilizing cobalt (Co) seems promising due to its excellent chromium retention capability [18,22–26].

To understand how the surface stability of the applied steel is affected and how the electrical performance of ceramic/composite materials in SOFCs operating at about 1073 K may be improved, it is necessary to

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obtain information on the mechanism responsible for the formation of the product of the reaction between the conductive coating and the metallic substrate. This is a key issue with regard to the application of steel as an interconnect in SOFCs.

In this study, the surface of the DIN 50049 stainless steel was coated with cobalt by means of the pulsed laser deposition (PLD) technique followed by 500 h of heat treatment in air at 1073 K, carried out in order to produce an oxide layer via a solid state reaction between Co and the steel components. The post-oxidation phase, chemical composition, and morphology of the reaction products were investigated, with a particular focus on the metallic substrate/coating interface. The effects of cobalt protection were discussed in terms of oxidation rate, electrical properties and chromium vaporization rate. Moreover, the possible mechanism for the observed oxidation behavior of the DIN 50049/Co composite layer was discussed.

2. Experimental

2.1. Preparation of steel substrate and coating process

The material used for the experiments was the commercial DIN 50049 ferritic steel from Valcovny Plechu a.s. Frydek-Mistek, Czech Republic, with the chemical composition of: Fe (Bal.), Cr (24.55 mass%), Mn (0.28 mass%), Si (0.74 mass%), Ni (0.99 mass%), C (0.04 mass%), P (0.03 mass%) and Ti (0.01 mass%). In the oxidation study, two types of samples cut from the supplied material were used: (1) rectangular plates with the dimensions of $20 \times 10 \times 1 \times 10^{-9}$ m^3 — used for oxidation kinetics and Cr-vaporization tests, and (2) square plates with a total area of 2×10^{-4} m^2 and a thickness of about 1×10^{-3} m — used for electrical resistance measurements. The surfaces of all specimens were ground with 100–1200 grit SiC papers, then polished with a 0.3 μm alumina slurry (OP-U Struers, Denmark), ultrasonically degreased, and finally washed in acetone and ethanol immediately prior to each use.

A metallic Co film was deposited on the DIN 50049 steel substrate at room temperature by means of PLD carried out in a multiport stainless steel vacuum chamber equipped with a gas inlet, a rotating multi-target and a heatable substrate holder using a Nd:YAG pulsed laser (NEOCERA, Germany) with a wavelength of 266 nm and with a laser fluence ranging from 6×10^{-4} to 7×10^{-4} J·m^{-2}. A frequency of 10 Hz and a laser pulse dwell time of 12 ns were applied. The target-to-substrate distance of 7×10^{-2} m was maintained. The laser ablation deposition was performed in a vacuum chamber equipped with a rotating target support and a substrate holder. The chamber was kept under dynamic vacuum (1.3×10^{-3} Pa) during the deposition process. To obtain a cobalt layer on the steel, a target prepared from spectral purity metal (Johnson Matthey Chemicals Ltd., UK), with a diameter of 1×10^{-2} m and a thickness of about 2×10^{-3} m, was used. A thin film was deposited on the polished surface of the DIN 50049 steel substrate. The time of deposition was 45 min., which amounted to 27,000 pulses at a substrate temperature of 298 K. The laser beam was incident at an angle of 45° on the target's surface. The rotating velocity of the ablated target averaged 5° per minute and the rotating velocity of the substrate averaged 21° per minute.

The coated samples were isothermally annealed at 1073 K in a batch-type furnace for 500 h, with air as the ambient atmosphere. The heating and cooling rates were 2 K·min^{-1}.

2.2. Coating characterization

The oxidation kinetics of coated and uncoated steel samples were investigated under isothermal conditions, for up to 500 h in air at 1073 K, using a thermogravimetric apparatus with a MK2-G5 vacuum Head Microbalance (CI Electronics Ltd., UK) with a sensitivity of 10^{-9} kg. The high-temperature thermogravimetric apparatus had been described previously [27].

The phase composition of the oxidized specimens was analyzed by means of X-ray diffraction (XRD) using the CuK$_\alpha$ radiation at a scan rate of 0.008° per step (X'Pert XRD diffractometer, PANalytical). Qualitative phase analyses were determined based on the Rietveld Profile Refinement Method, using HighScore Plus software (PANalytical) coupled with the X'Pert diffractometer and the standard PCPDFWIN v.2.3 data set.

An FEI Nova NanoSEM 200 scanning electron microscope coupled with an EDAX Genesis XM X-ray microanalysis system featuring the EDAX Sapphire Si(Li) energy-dispersive X-ray spectroscopic (EDS) detector was used to perform a detailed examination of the morphology and chemical composition of the oxide scales grown on the studied steel. The scanning electron microscopic (SEM) observations were carried out using a secondary electron (SE) in low vacuum conditions (60 Pa) and at an accelerating voltage of 18 kV. Weight and atomic percentages of elements were estimated via the normalized standardless EDAX-ZAF quantitative method. The samples were covered with a carbon layer. Surface topography studies of the coated steel samples were also performed by applying the Bruker Multimode 8 atomic force microscope (AFM). All surface images were obtained in the semi-contact Peak Force Tapping mode using silicon nitride probes covered with a reflective Au coating, with a 2-nm radius of the curvature of the tip.

Electrical resistance measurements of the studied samples were conducted by means of the 2-probe 4-point direct current method, using an external current source. Two types of studies were performed. The first type was based on a function of oxidation time at 1073 K, under a constant current density of 3×10^3 A·m^{-2}. The second type included a function of temperature in the range from 873 to 1073 K, using a current intensity of 1×10^{-2} A and laboratory air. The resistance of all studied samples was measured after the entire oxidation process had ended. Both sides of the oxidized samples were covered with Pt paste (Heraeus) followed by placing Pt meshes with a surface area of 1.9×10^{-5} m^2 on top of the paste. The sample prepared in this 'sandwich' system was placed between two-plane Pt electrodes, and the voltage drop was measured under direct current (and with polarity reversal) using the ZS-2002 programmable power supply manufactured by JOTA (Poland). The current drop for each sample was measured by means of an HP digital multimeter (34401) with 0.3% precision. Sample resistance was recorded at the given temperature every 10 min. The temperature was then increased by 50 K and the sample was equilibrated at this increased temperature for 1 h. The apparatus used to measure the electrical resistance (R) and the sample preparation procedure are described in [28]. The electrical resistance of an oxidized specimen is usually measured in terms of its area-specific resistance (ASR), which is defined as the product of resistance and the nominal contact surface area of the oxide and the steel. Due to the symmetrical design of the sample, the ASR of the samples was calculated based on the obtained resistance values using the following formula (1):

$$ASR = \frac{R \cdot A}{2} \tag{1}$$

where R is the electrical resistance [Ω] and A is the surface area of the Pt layer [m^2].

Chromium vaporization rate tests of the studied samples were performed for 72 h in humidified air ($p(H_2O) = 9.7 \times 10^3$ Pa) at 1073 K, in an apparatus with a construction similar to the one proposed by Kurokawa et al. [29]. The details of the apparatus used for Cr-vaporization rate tests and the preparation procedure of the studied samples had been described previously [30]. The concentration of chromium in the obtained aqueous solution containing the dissolved Cr was determined by means of the atomic absorption spectroscopy method.