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Chromium vaporization from mechanically deformed pre-coated interconnects in Solid Oxide Fuel Cells

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HIGHLIGHTS

- Cr vaporization from real Solid Oxide Fuel Cell interconnects was measured.
- Stamping pre-coated Co coated steel induced large cracks in the coating.
- The cracks healed during exposure forming a top layer of $(Co,Mn)_3O_4$.
- As a result of the rapid healing, no increase in Cr vaporization was measured.

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ABSTRACT

Cathode poisoning, associated with Cr evaporation from interconnect material, is one of the most important degradation mechanisms in Solid Oxide Fuel Cells when Cr_2O_3-forming steels are used as the interconnect material. Coating these steels with a thin Co layer has proven to decrease Cr vaporization. To reduce production costs, it is suggested that thin metallic PVD coatings be applied to each steel strip before pressing the material into interconnect shape. This process would enable high volume production without the need for an extra post-coating step. However, when the pre-coated material is mechanically deformed, cracks may form and lower the quality of the coating. In the present study, Chromium volatilization is measured in an air-3% H_2O environment at 850 °C for 336 h. Three materials coated with 600 nm Co are investigated and compared to an uncoated material. The effect of deformation is investigated on real interconnects. Microscopy observations reveal the presence of cracks in the order of several μm on the deformed pre-coated steel. However, upon exposure, the cracks can heal and form a continuous surface oxide rich in Co and Mn. As an effect of the rapid healing, no increase in Cr vaporization is measured for the pre-coated material.

1. Introduction

High electrical conversion efficiency, clean emissions and the possibility to utilize several types of fuels, such as hydrogen and carbon-based fuels, are some of the great advantages of Solid Oxide Fuel Cell (SOFC) technology [1]. To increase the output of electricity, several cells are electrically connected in series, often referred to as a fuel cell stack. A key component in the stack is the interconnect which separates the air and fuel compartments of neighboring cells and also connects them electrically. The interconnect, also called a bipolar plate, must be gas tight, electrically conductive and stable in both high pO_2 (air on the cathode side) and low pO_2 (fuel on the anode side) environments [2,3]. Moreover, it must be shaped in a certain way that allows for gas distribution. Today, ferritic stainless steels have become the most popular choice of interconnect material for planar SOFC applications [4] that operate at 600–900 °C. The stability of such steels depends on the formation of a protective oxide that separates the oxidizing gas from the steel. Due to the requirement for good electrical conductivity of the interconnect material, steels that form a protective Al_2O_3 layer must be excluded, which leaves Cr_2O_3-forming steels as the best option. However, on the cathode side, which contains both oxygen and water vapor, Cr(VI) species, such as $CrO_2(OH)_2$, vaporize from the Cr-rich surface oxide scale [5–8]. The volatile Cr(VI) species are then transported to the cathode where they may either be reduced back to Cr(III) at the Three Phase Boundary (TPB), forming deposits which block the

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electrochemical oxygen reaction process, or directly react with other stack components [9–12]. Both cases lead to fast stack degradation, and for this reason, it is of great importance to minimize Cr vaporization.

Applying ceramic or metallic coatings to reduce Cr vaporization has become the most widespread solution, and several coating systems have been studied within the last decade. One of the most promising candidates is the $(Co,Mn)_3O_4$ coating system. Such a coating can be applied utilizing various techniques such as spray drying, dip-coating, screen printing, aerosol spray deposition, plasma spraying or by Physical Vapor Deposition (PVD) [13–21]. Another alternative is to coat the steel with metallic Co which forms $(Co,Mn)_3O_4$ upon oxidation due to the outward diffusion of Mn from the steel [22–32]. Applying metallic coatings also eliminates the extra heat treatment that is necessary to produce a dense coating when techniques such as spray-drying, dip-coating and screen printing are utilized. For SOFCs to become economically attractive, their cost must be reduced significantly. Today most coated interconnect materials are manufactured in two separate steps: (1) stamping the uncoated steel into an interconnect shape and (2) coating the deformed steel plate (post-coating). This two-step batch coating concept is rather inefficient for mass production, and for this reason alternative processes should be explored. Alternatively, large amounts of steel sheet can be pre-coated and subsequently shaped into interconnects allowing for much more efficient large scale production, and as a consequence, lower overall costs. In the present study, thin PVD coatings were studied that were applied by Sandvik Materials Technology using a PVD process. With this technique several hundreds of meters can be coated in an industrial scale roll-to-roll technique enabling high volume production without the need for an extra coating step after the steel has been shaped into interconnects [33]. Earlier studies on undeformed materials have shown that thin PVD films of metallic Co significantly reduce Cr vaporization [23–26]. However, delamination of the coating as well as the formation of large cracks may occur when the pre-coated steel strip is shaped into interconnects. This may have a significant effect on Cr vaporization, which would reduce stack lifetime. For this reason, the aim of this study is to investigate whether the mechanical deformation process will lead to increased corrosion and Cr vaporization of the interconnect material.

2. Materials and methods

All exposures were performed on either uncoated or 600 nm Co coated Crofer 22 APU foils. Table 1 shows the chemical composition of Crofer 22 APU. Coatings were prepared by Sandvik Materials Technology using a Physical Vapor Deposition (PVD) process, and mechanical deformation was conducted utilizing a Topsoe Fuel Cell interconnect design. Four types of materials were analyzed: (1) uncoated and undeformed, (2) Co coated and undeformed, (3) deformed and subsequently coated (post-coated) and (4) pre-coated and subsequently deformed (see Fig. 1). Prior to exposure, all samples, with a steel thickness of 0.3 mm, were cut into 15 × 15 mm^2 coupons and cleaned with acetone as well as ethanol in an ultrasonic bath.

All samples were isothermally exposed to air-3% H_2O at 850 °C for up to 336 h. 850 °C was chosen as exposure temperature to accelerate the test somewhat. The flow rate was 6000 sml min^{-1} corresponding to 27 cm s^{-1}. The 3% water vapor level in the gas was achieved by bubbling dry air through a heated water bath connected to a condenser containing water at a temperature of 24.4 °C. The samples (three coupons per exposure) were placed parallel to the gas stream. Downstream of the samples, the gas was lead through a silica glass denuder tube. To collect the volatile Cr(VI) species, this denuder tube was coated with Na_2CO_3, which reacts with $CrO_2(OH)_2(g)$ according to the following reaction:

$$CrO_2(OH)_2(g) + Na_2CO_3(s) \rightarrow Na_2CrO_4(s) + H_2O(g) + CO_2(g)$$

The denuder tube could be replaced regularly and rinsed with distilled water without affecting the samples. The amount of vaporized Cr was then quantified by spectrophotometry using an Evolution 60S Thermo Scientific instrument. A more detailed description of the denuder technique and the experimental setup can be found elsewhere [25].

Mass gain was recorded as a function of time after each isothermal exposure by calculating the average mass gain from the three coupons exposed simultaneously. A six-decimal place micro balance (Metler Toledo XP6) was utilized for this purpose. The microstructure and chemical composition of each sample surface was analyzed in an FEI Quanta 200 FEG Environmental Scanning Electron Microscope (ESEM) equipped with an Oxford Instruments X-Max^N Energy Dispersive X-ray spectroscopy (EDX) detector and INCAEnergy software. High vacuum mode and an accelerating voltage of 15 kV were used for all top view images. Cross sections were prepared from two of the samples: pre-coated samples exposed for 24 h and 336 h. The cross section of the 336 h exposed sample was prepared mechanically whereas Focused Ion Beam (FIB) milling and lift-out technique were utilized to prepare a thin specimen from the pre-coated sample which had been exposed for 24 h. For this purpose, an FEI Versa 3D DualBeam Focused Ion Beam/Scanning Electron Microscope (FIB/SEM) was used. To protect the sample from ion beam damage during milling, two layers of Pt were deposited on the area of interest, first using an electron beam followed by an ion beam induced deposition. To minimize the amount of ion beam damage and amorphization, ion milling was carried out in a gradually decreasing beam current in the following steps: 850, 450 and 250 pA at 30 kV and 45 pA at 5 kV.

Table 1
Composition of the studied steel Crofer 22 APU in weight %. The values are specified according to the manufacturer for received batches.

Material	Manufacturer	Fe	Cr	Mn	Si	Ti	Add
Crofer 22 APU	ThyssenKrupp VDM	Bal.	22.9	0.38	0.01	0.06	La

3. Results and discussion

3.1. Gravimetric analysis

Mass gain and Cr vaporization, as a function of time of the isothermally exposed samples in air-3% H_2O at 850 °C, are shown in Fig. 2. All Co coated materials showed a rapid gain in mass within the first few minutes of exposure time compared to the uncoated material. This mass gain of approximately 0.2 mg cm^{-2} corresponds to oxidation of the Co coating and the formation of Co_3O_4 [24]. Furthermore, all coated samples showed similar oxidation behavior which indicates that shaping the material into an interconnect had not influenced the oxidation kinetics during the experiment period. After 336 h of exposure, all the coated materials gained 0.9–1.0 mg cm^{-2} in mass whereas the uncoated material had only gained 0.5 mg cm^{-2} in mass. The mass gain for the uncoated material after 336 h was lower than the three coated samples even when the 0.2 mg cm^{-2}, corresponding to the initial oxidation of the metallic Co coating, was compensated. The main reason for this is associated with the much higher rate of Cr vaporization for the uncoated material [24,34–36].