Chromium volatility of coated and uncoated steel interconnects for SOFCs

C. Collins [a], J. Lucas [a], T.L. Buchanan [a], M. Kopczyk [a], A. Kayani [a], P.E. Gannon [a], M.C. Deibert [a], R.J. Smith [a,*], D.-S. Choi [b], V.I. Gorokhovsky [c]

[a] Montana State University, Bozeman, MT 59717, United States
[b] Kangwon National University, Republic of Korea
[c] Arcomac Surface Engineering, LLC, Bozeman, MT 59715, United States

Available online 13 November 2006

Abstract

The requirements of low cost and high-temperature corrosion resistance for bipolar interconnect plates in solid oxide fuel cell stacks has directed attention to the use of steel plates with more oxidation resistant compositions. However, volatile Cr species from the Cr_2O_3-based oxide scales on these steels find their way to the triple-phase boundary, leading to rapid degradation of fuel cell performance. Coatings can serve not only to slow oxidation rates, but also as diffusion barriers for the Cr-derived species from the steel, slowing the degradation process. We have developed a relatively quick, quantitative procedure using Rutherford Backscattering Spectroscopy (RBS) to obtain measurements of the Cr vaporization rates. Chromium-containing vapors from the steel coupons in a tube furnace at 800 °C were transported with various flow rates of humid air to a Si wafer at ∼ 110 °C near the end of a quartz tube in a tube furnace, where the vapors adsorbed on the Si surface. The wafers were subsequently analyzed for Cr surface concentrations using Rutherford backscattering. Results are presented for 430 SS and for CroferAPU22, the latter with and without a Co–Mn–O spinel coating deposited using hybrid filtered-arc deposition assisted electron beam physical vapor deposition. Separate experiments with Cr_2O_3 powder as the vapor source established the quantitative reliability of this approach.
© 2006 Published by Elsevier B.V.

1. Introduction

Solid oxide fuel cells (SOFC) are becoming increasingly attractive as a way of converting chemical energy into electrical energy by means of the electrochemical combination of hydrogen and oxygen via an ion-conducting solid oxide electrolyte. The operational requirements of high ionic conductivity and good catalytic performance in the fuel cell must be balanced against the practical requirements of low cost and high-temperature corrosion resistance for components in the fuel cell stack [1]. Of particular interest in our work is the bipolar plate serving as the current collector or interconnect between adjacent cells of the SOFC stack. The interconnect must not only retain low electrical resistivity throughout the operating lifetime of the fuel cell, but must also have good surface stability, necessitating that thermal expansion and other physical properties be compatible with the materials in the stack [2]. Doped $LaCrO_3$ plates have worked well for cells operating at 1000 °C, but suffer from

high cost as well as difficulties in fabrication. The recent trend towards lower operating temperatures (650–800 °C) may enable the use of more cost-effective materials. A thorough evaluation of several heat-resistant alloys with a variety of compositions led to the conclusion that it would be difficult for most traditional alloys to meet the material requirements of long-term operation above 700 °C [3]. Furthermore, it has been shown repeatedly that at these high operating temperatures volatile Cr containing species can enter the gas stream and cause cell degradation as a result of deposition at electrode or electrolyte interfaces [4]. It is believed that the vaporization is the result of a water surface reaction at the chromia scale of the cathode in air [5]. To meet the demanding requirements of the SOFC application, either new alloys need to be developed, or surface engineering of existing alloys is required [3]. Among candidate materials in the former category is Crofer22 APU, an Fe–Cr based ferritic stainless steel with additional manganese (available from ThyssenKrupp VDM). The present work falls into the latter category of surface engineering, namely, the use of coatings to improve oxidation resistance while maintaining acceptably low resistivity values. An appropriate coating may serve not only as a barrier to the

1. Compressed Air   4. Quartz Tube   7. Substrate
2. Flow Meter   5. Tube Furnace 8. Water Cooled Heat Sink
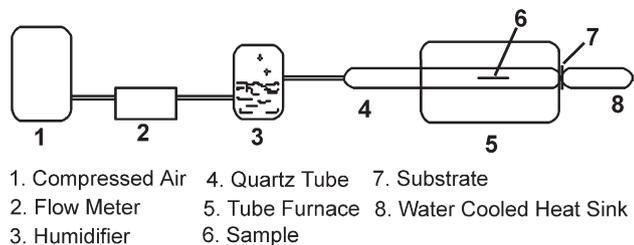3. Humidifier   6. Sample

Fig. 1. Experimental setup for measuring chromium vaporization rates.

diffusion of oxygen into the interconnect material, but also as a barrier to inhibit the diffusion of elements from the steel to the surface of the interconnect. Recent studies have focused on the performance of manganese cobaltite spinel (Mn, Co)$_3$O$_4$ protection layers [6–8]. The use of coatings for this application brings with it an additional set of problems, namely, guaranteeing the integrity of the coating with respect to adhesion, wear resistance, and detrimental effects associated with interdiffusion between coating and substrate material. On the other hand, using coatings enables the use of inexpensive alloys that would otherwise be ruled out because of their poor oxidation resistance or high Cr volatility at operating temperatures.

This paper describes a reliable and fast method to quantify and compare the chromium vaporization rates from various types of coated and uncoated steel surfaces. A few groups have developed transpiration methods for measuring chromium vaporization rates from the surfaces of candidate interconnect materials. These methods involve trapping Cr vapors in a glass tube and/or water bath, dissolving Cr species with nitric acid from the glass surfaces of components, and measuring Cr concentrations with atomic absorption spectroscopy [9,10]. In the method presented here, the Cr vapor is passed over the surface of a Si wafer, and the amount of Cr condensed on the Si surface is measured using Rutherford backscattering spectroscopy (RBS). This method has advantages in that it is quantitative, non-destructive, fast, and very sensitive to heavy elements. As shown here, it is straightforward to measure the Cr volatility from a surface as a function of time. As with any quantitative method, care is required to determine the collection efficiency, but measurements of the collected amounts of Cr are straightforward, requiring no standards or reference measurements.

To evaluate the reliability of the method used here, Cr$_2$O$_3$ powder was used as a high surface area Cr source to determine appropriate flow rates for the humidified air. The data can be compared to other results in the literature to determine whether this method of Cr collection provides quantitative measurements, and the fraction of the Cr captured on the Si wafer. However, there are large uncertainties in the reported values for the thermodynamic properties related to Cr vaporization, making such a determination somewhat uncertain [9].

2. Experimental procedure

Fig. 1 shows a sketch of the experimental configuration. The steel sample (6), typically a few cm^2 in area, is located at the center of a quartz tube (4) in a tube furnace (5) with programmable temperature control. Both surfaces of the steel cou-

pon are exposed to the humid air passing through the tube. Compressed air from a tank (1) flows through a bubbler (3) at room temperature, and is monitored by a flow meter (2). The tank regulator provides a steady flow through the bubbler for adding humidity to the air. Although relative humidity was not measured for these early results, we noted condensation on the walls of the tubing leading to the quartz tube, and estimate the humidity content to be ~3% at room temperature, based on procedures reported in the literature (6). Volatile chromium species vaporized from samples heated to 800 °C are transported and collected on a commercial silicon wafer substrate (7), held near 110 °C on a water-cooled copper heat sink (8). The Si is attached to the Cu with carbon tape. It was found that Cr does not deposit on Si surfaces placed inside the oven, near the steel coupon. Therefore the Si coupon is held at a much lower temperature to increase Cr collection, just inside the end of the tube furnace. The substrate and heat sink are held above the boiling point to prevent water in the humid air from condensing in droplets on the Si surface. The water-cooled Cu heat sink fits snugly inside the quartz tube. To maintain the flow of air through the quartz tube, four small exit channels are cut around the circumference of the Cu heat sink. The fractional area of these openings relative to the tube cross section is quite small, so we expect some type of turbulent flow near the tube boundary. We also expect that some Cr vapor escapes the tube through these small channels, and experiments are underway to quantify the fraction of Cr collection for this configuration. Some discoloration of the walls of the quartz tube was observed near the four exit channels, possibly due to Cr condensation on the tube walls, after several hundred hours of operation. Flow rates, oven temperature, sample and substrate temperatures, and heat-sink water coolant temperatures are monitored with a data acquisition system.

For most measurements, two separate Si coupons were mounted side-by-side on the Cu heat sink, using carbon tape. Typically, one coupon remained mounted for the duration of an
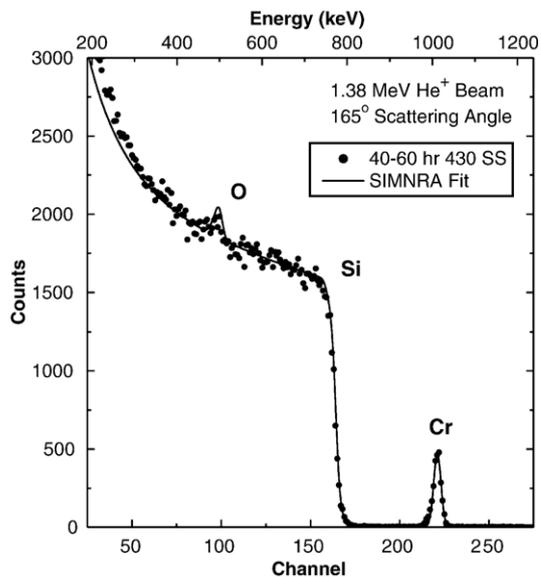

Fig. 2. RBS spectrum to determine the amount of chromium collected on silicon wafer.
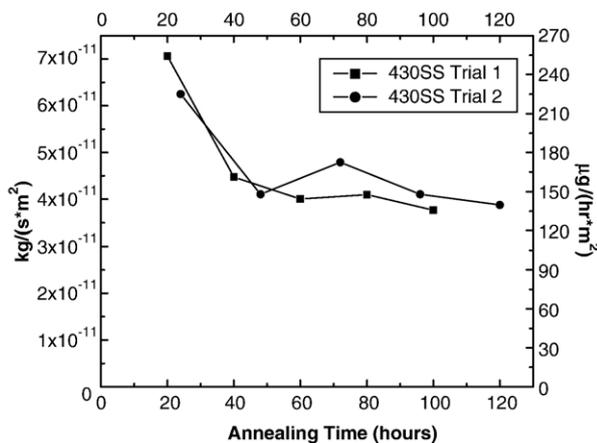
Fig. 3. Repeated experiment to measure Cr volatility from two 430 stainless steel coupons.

Fig. 4. Chromium collected from Cr_2O_3 powder as function of flow rate for humid air.

entire experiment, while the other coupon was replaced with a fresh piece of Si every 20–25 h during the run. The Cr concentration was measured with RBS on each of the removed Si pieces, giving the time evolution of condensed Cr vapor originating from the steel. The integrated amount of Cr from these measurements was then compared to the total Cr condensed on the Si coupon left on the Cu heat sink for the duration of the run. This comparison allowed us to determine if there were Cr coverage-dependent or other time dependent sticking coefficients for the Cr adsorption on the Si wafers. When using Cr_2O_3 powder for the sample, the summation of the Cr amounts for the individual coupons was 80–95% of the total Cr collected on the fixed Si coupon. However, for measurements with the coated steel as the source, the total Cr on the stationary wafer was 65% of that summed from the several removed wafers. The source of this discrepancy is still not clear, but it is important to note that these two situations represent quite different chromium vaporization rates, as seen in the results presented below. We also verified that the Cr concentration condensed on the wafer was quite uniform over the area of the wafer, which could be nearly as large as the diameter of the quartz tube and Cu heat sink for some measurements.

Experiments with different volumes of Cr_2O_3 powder were performed to determine the appropriate flow rates for equilibrium and non-equilibrium conditions above the powder. Humid airflow of 1000 ml/min provides non-equilibrium conditions for the chromium transport as shown in the next section, and was used for measurements from the steel surfaces.

The amount of chromium collected on the silicon was measured using RBS, as shown in Fig. 2. Since the Rutherford cross section is known, this method can be quantitative. The spectrum shows the number of He ions scattered from the sample surface as a function of the backscattered ion energy for a scattering angle of 165°. Peaks representing heavier elements are at a higher channel, representing higher backscattered ion energy. Elements on the surface of the Si that have a lighter mass than the substrate will form a peak on top of that for the thick Si substrate. The area under the peak for each element represents the quantity of that element on the surface, and is converted to an areal density (at/cm^2) using the Rutherford
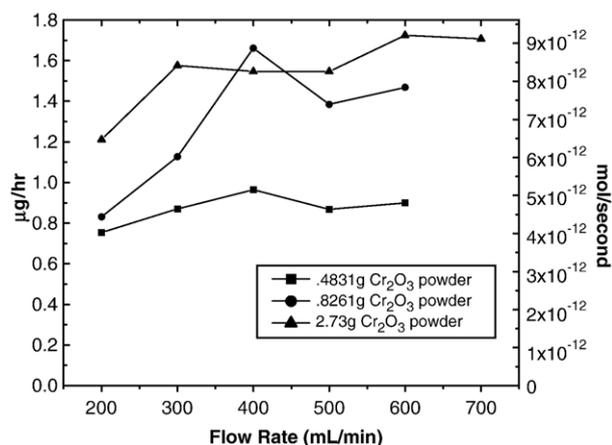
cross section and experimental parameters. The spectrum of Fig. 2 shows the backscattered signal from the Si substrate, with the Si surface represented by scattered ions in the edge at channel 162. Oxygen on the surface is indicated by the peak at channel 99. Chromium on the surface is determined from the area of the peak at channel 223. By choosing a substrate with mass less than that of Cr, the Cr signal appears in a region of zero background, giving the measurement sensitivity to sub-monolayer amounts of Cr, yet having a relatively unlimited upper bound. Quantification is accomplished using the SIMNRA program [11], providing a value for the number of Cr atoms per cm^2 on the Si surface. Since we know the cross sectional area of the quartz tube, and we verified that Cr condensation is quite uniform over this area, and that little, if any, Cr condenses on the hot walls of the quartz tube inside the furnace, the amount of Cr vapor leaving the sample can be calculated. The value obtained will be deficient by the amount of Cr leaving the tube through the four small channels around the heat sink. This fractional collection will be determined in future experiments. However, as we show below, the results are quite reproducible, making measurements of relative chromium volatility quite reliable.
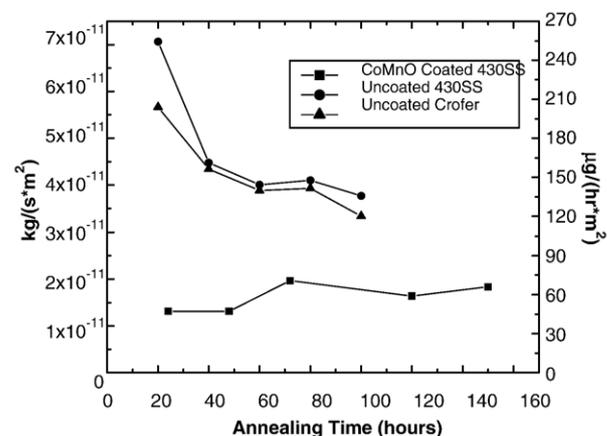

Fig. 5. Cr vaporization rates of coated and uncoated steels as a function of time at 800 °C in humid air.

3. Results and discussion

3.1. Establishment of reproducibility

Factors such as flow rate, humidity in the air, and substrate or sample condition may all affect Cr collection. Fig. 3 shows the results for two separate runs using two uncoated 430 stainless steel coupons. Each data point represents a measurement of Cr accumulated on the Si wafer during the time interval between that point and the previous point, e.g. 20-hour intervals in trial 1 of Fig. 3. The vertical scale was calculated assuming that the total Cr vaporized from the source during a given time interval was collected over the area of the quartz tube diameter at the heat sink. It is clear that the measurement was quite reproducible for two different samples. Future experiments involving the collection of exhaust gas exiting through the four side channels will determine the ratio of Cr collected to that escaping the tube, resulting in an absolute, quantitative measurements of Cr vaporization rates.

3.2. Dependence of Cr collection on flow rate

To measure the actual value of Cr volatility from a source, it is important to capture all of the vaporized Cr from the sample. When the flow rate is low, the vapor will be in equilibrium above the source, and any small amount of vapor removed by transport to the end of the tube will be quickly replenished at the source. Thus, the amount collected will increase linearly with flow rate, as reported in the literature [9]. However, if the flow rate is sufficiently high, all of the Cr vapor coming off the source is transported to the end of the tube, and increasing the flow does not result in additional amounts of Cr. Thus the curve of collected Cr as a function of flow rate should increase linearly to a plateau value. Fig. 4 shows our measurements for three different quantities of Cr_2O_3 powder (99% pure, metals basis) heated to 800 °C in humid air. The powder was placed loosely in a ceramic boat and transferred to the quartz tube. For the smallest amount of powder (solid squares) the plot of collected Cr vs. flow rate is relatively flat, indicating that all the vapor leaving the powder is being transported to the collection point, even for the lowest flow rate of 200 ml/min, i.e. a non-equilibrium condition. Doubling the amount of powder used (solid circles) increased the vaporization rate as expected, and the curve increases to a saturation value as flow rate is increased, although the saturation level is a bit less than double that for the smaller amount of powder. Finally, we increased the amount of powder by a factor of five. There is an increase in Cr vaporization rate for the lowest flow rate, but the saturation level remains the same, suggesting that now some other factor is limiting the rate of Cr vaporization. We believe this limit reflects the amount of humidity present in the air flow, but this needs to be checked in future experiments.

3.3. Chromium vaporization rates for coated and uncoated steel

Samples of uncoated 430 SS (surface area = 36.43 cm^2) and CroferAPU22 (37.56 cm^2) were tested for Cr volatility, as shown in Fig. 5. Annealing was done in five 20-hour intervals for a total time of 100 h. After each 20-hour interval, the steel was slowly cooled to room temperature, and the Si substrate was replaced, before beginning the next 20-hour cycle. In Fig. 5, each data point represents average vaporization rate over the prior 20-hour interval. The results show nearly identical vaporization rates for the two steels. A small piece of 430 SS (4.37 cm^2) with a Co–Mn–O coating was also tested with 24-hour intervals, keeping the sample at 800 °C throughout the duration of the experiment. The coating was applied by Arcomac Surface Engineering, Bozeman, MT, to both sides of the coupon using hybrid filtered-arc deposition assisted electron beam physical vapor deposition. The target was a sintered pellet with nominal stoichiometry of $Co_{1.5}Mn_{1.5}O_4$, containing two phases identified by X-ray diffraction: $CoMn_2O_4$ and Co_2MnO_4. The coated surface showed a smaller vaporization rate, by about 50%, at the end of the experiment, after 150 h.

4. Conclusion

We have demonstrated a procedure using ion beam analysis (RBS) that makes possible the rapid determination of the time-dependent Cr volatility for steels heated to 800 °C in humid air. A silicon substrate has a satisfactory sticking coefficient for collecting chromium, although further experiments are needed to quantify the fractional amount of chromium collected in this design. The technique is highly reproducible, fast, and can be quantitative. The chromium vaporization rates of uncoated 430 stainless steel and CroferAPU22 have been compared and found to be similar for up to 100 h. A Co–Mn oxide coating on 430 SS reduced the volatility by about a factor of two. Accurate rates for coated steels may be more difficult to establish when the amount of chromium collected is small, but chromium vaporization can still be observed.

References

[1] B.C.H. Steele, A. Heinzel, Nature 414 (2001) 345.
[2] Z.G. Yang, J.W. Stevenson, P. Singh, Adv. Mater. Process. 161 (6) (2003) 34.
[3] Z. Yang, K.S. Weil, D.M. Paxton, J.W. Stevenson, J. Electrochem. Soc. 150 (9) (2003) A1188.
[4] S.P. Jiang, J.P. Zhang, X.G. Zheng, J. Eur. Ceram. Soc. 22 (2002) 361.
[5] K. Hilpert, D. Das, M. Miller, D.H. Peck, R. Weiβ, J. Electrochem. Soc. 143 (11) (1996) 3642.
[6] Z. Yang, G. Xia, J.W. Stevenson, Electrochem. Solid-State Lett. 8 (3) (2005) A168.
[7] Y. Larring, T. Norby, J. Electrochem. Soc. 147 (9) (2000) 3251.
[8] X. Chen, P.Y. Hou, C.P. Jacobson, S.J. Visco, L.C. De Jonghe, Solid State Ionics 176 (2005) 425.
[9] C. Gindorf, L. Singheiser, K. Hilpert, J. Phys. Chem. Solids 66 (2005) 384.
[10] C. Gindorf, L. Singheiser, K. Hilpert, Steel Res. 72 (11/12) (2001) 528.
[11] M. Mayer, SIMNRA user's guide, Technical Report IPP 9/113, Max-Planck-Institut fur Plasmaphysik, Garching, Germany, 1997.