Evaluation of Solid Oxide Fuel Cell Interconnect Coatings: Reaction Layer Microstructure, Chemistry and Formation Mechanisms

Neal J. Magdefrau
neal.magdefrau@gmail.com

Follow this and additional works at: http://digitalcommons.uconn.edu/dissertations

Recommended Citation
http://digitalcommons.uconn.edu/dissertations/106
Evaluation of Solid Oxide Fuel Cell Interconnect Coatings: Reaction Layer Microstructure, Chemistry and Formation Mechanisms

Neal J. Magdefrau, Ph.D.

University of Connecticut, 2013

The implementation of improved electrolyte materials have led to modern solid oxide fuel cells (SOFCs) which operate at lower temperatures (600-800 °C) than previously possible. The lower operating temperatures enable the use of chromia forming metallic interconnects which are less expensive and more manufacturable than their ceramic counterparts. However, poor oxidation resistance and the evolution of volatile chromia species currently limit the lifetime of the SOFC stack. As such, protective conductive ceramic coatings such as Mn$_{1.5}$Co$_{1.5}$O$_4$ (MCO) are necessary to protect the underlying alloy and prevent chromia species from poisoning the SOFC cathode.

In this thesis, a study of microstructural changes of bare and MCO coated Crofer 22 APU and Haynes 230 alloys is presented. Oxidation studies on bare Crofer 22 APU heat-treated at 1050 °C prior to oxidation showed that samples with a larger starting grain size had up to a 3.5X reduction in oxidation kinetics. In addition, heat treatment prior to oxidation was shown to promote the formation of an external MnCr$_2$O$_4$ protective spinel. MCO coated Crofer 22 APU was examined after various exposure times in air at 800 °C. Detailed Focused Ion Beam (FIB) and Transmission Electron Microscopy (TEM) studies revealed the presence of a thick (Mn,Co,Cr,Fe)$_3$O$_4$ cubic spinel reaction layer (RL).
Similarly, bare Haynes 230 oxidation kinetics was examined and shown to have a parabolic rate constant, \( k_g \), of \( 8.9 \times 10^{-9} \text{ mg}^2\text{cm}^{-4}\text{s}^{-1} \), which is nearly an order of magnitude slower than the oxidation kinetics of Crofer 22 APU. MCO coated Haynes 230 also forms a spinel RL, but this is approximately 3-5X thinner than RLs formed on MCO coated Crofer 22 APU exposed under identical oxidation conditions. Previously developed equivalent circuit models have shown that the RLs reported here can have a profound impact on the oxidation kinetics of the coated interconnect system. The formation mechanisms, RL crystal structure, chemistry and implications for long-term SOFC performance are discussed.

Evaluation of Solid Oxide Fuel Cell Interconnect Coatings: Reaction Layer Microstructure, Chemistry and Formation Mechanisms

Neal J. Magdefrau

B.S.E, University of Connecticut, 2005
M.S., University of Connecticut, 2006

A Dissertation
Submitted in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy
at the University of Connecticut

2013
Copyright by

Neal J. Magdefrau

2013
Evaluation of Solid Oxide Fuel Cell Interconnect Coatings: Reaction Layer Microstructure, Chemistry and Formation Mechanisms

Presented by
Neal J. Magdefrau, B.S.E, M.S.

Major Advisor
Mark Aindow

Associate Advisor
S. Pamir Alpay

Associate Advisor
Prabhakar Singh

University of Connecticut
2013
Acknowledgements

I’d like to thank everyone who has contributed in part to this dissertation. First, I would like to thank my advisory committee, especially Dr. Mark Aindow who has been an invaluable advisor and role model to me since I was a freshman in college. His passion for quality experimental work and scientific writing has set the bar high at every level of my educational career. I’d also like to thank my associate advisors, Dr. Pamir Alpay and Dr. Prabhakar Singh for their useful discussions and contributions to this work.

A special thanks to Dr. Roger Ristau for his insights and help with FIB experiments. I would also like to thank the current members of Dr. Aindow’s research group for their help and encouragement along the way: Mr. Mauricio Gordillo, Mr. Christian Ayala, Mr. Louis Gambino, Mr. Sriram Vijayan and Mr. Haibo Yu. I would like to thank my research group at UTRC who has contributed to and inspired this work in many ways. A special thanks to Mr. Lei Chen for his numerous detailed technical discussions and for his help getting this research started. I would also like to thank Dr. Ellen Sun and Dr. John Yamanis for their helpful contributions to publications.

Last but not least I would like to thank my family; my parents for instilling in me that I could do anything that I put my mind to. To my wife Michelle, I cannot put into words how grateful I am to you. Completing this thesis would not have been possible without the many sacrifices that you made. As I have learned over the past years a part-time PhD is by no means a one-person endeavor and I owe much of the completion of this to my loving and supporting wife.
Preface

The enclosed thesis is comprised of research performed collaboratively at the University of Connecticut and United Technologies Research Center. This work is entirely original and has not been previously used for the completion of a degree at this or any other university. The work enclosed was completed on a part-time basis from 2009-2013. The majority of this work was paid for by the National Science Foundation under Grant No. 1100427. Chapters 4, 5 and 6 are taken from original published works by the current author and are referenced below:


Chapter 6: N.J. Magdefrau, L. Chen, E.Y. Sun, M. Aindow, The Effect of Mn$_{1.5}$Co$_{1.5}$O$_4$ Coatings on the Development of Near Surface Microstructure for Haynes 230 Oxidized at 800° C in Air. (Recently submitted for publication).
Table of Contents

List of Figures............................................................................................................................................... v
List of Tables ................................................................................................................................................ x

Chapter 1: Interconnect Alloys for Solid Oxide Fuel Cell ................................................................. 1
  1.1 Introduction to Solid Oxide Fuel Cells (SOFCs) ........................................................................ 1
  1.2 SOFC Interconnect Alloy Requirements ................................................................................. 2
  1.3 Typical SOFC Interconnect Alloys ............................................................................................... 4
    1.3.1 Ni-based Superalloys ................................................................................................................. 4
    1.3.1.1 Oxidation Resistance ............................................................................................................ 5
    1.3.1.2 Chemical Compatibility and Coefficient of Thermal Expansion (CTE) ............................ 5
    1.3.1.3 Mechanical Properties ......................................................................................................... 6
    1.3.2 Ferritic Stainless Steels ............................................................................................................ 7
    1.3.2.1 Coefficient of Thermal Expansion (CTE) .......................................................................... 7
    1.3.2.2 Oxidation Resistance and Conductivity .............................................................................. 8
    1.3.2.3 Chemical Compatibility ....................................................................................................... 12
    1.3.2.4 Mechanical Properties ....................................................................................................... 13
  2.1. Introduction to Coatings ........................................................................................................... 22
  2.2 Types of SOFC Interconnect Coatings ....................................................................................... 24
    2.2.1 Spinel Coatings ....................................................................................................................... 24
    2.2.2 Perovskite Coatings ............................................................................................................... 26
    2.2.3 Reactive Element Oxide Coatings ......................................................................................... 27
  2.3 Methods of Coating Application ............................................................................................... 27
    2.3.1 Magnetron Sputtering ............................................................................................................ 28
    2.3.2 Electroplating .......................................................................................................................... 29
    2.3.3 Metal-Organic Chemical Vapor Deposition (MOCVD) ......................................................... 30
    2.3.4 Slurry Coating Processes ....................................................................................................... 31
  2.4 Kinetics and Transport in Coated Alloy Systems ...................................................................... 32
    2.4.1 Oxidation Kinetics of Chromia Formers ............................................................................... 32
    2.4.2 Oxidation Kinetics of Coated Alloy Systems ....................................................................... 35

Chapter 3: Experimental Method ........................................................................................................... 42
  3.1 Preparation of Mn1.5Co1.5O4 Slurry ........................................................................................... 42
  3.2 Slurry Coating of Crofer 22 APU and Haynes 230 Coupons .................................................... 42
  3.3 Heat Treatment Prior to Oxidation of Bare Crofer 22 APU ....................................................... 43
  3.4 Reaction Layer Studies on MCO Coated Crofer 22 APU ......................................................... 45
  3.5 Reaction Layer Studies on MCO Coated H230 ......................................................................... 47

Chapter 4: Crofer Oxidation and Alloy Microstructural Effects ......................................................... 49
  4.1 Introduction/Preamble .................................................................................................................. 49
  4.2 Results .......................................................................................................................................... 51
    4.2.1 Pre-Heat Treatment Effect on Alloy Microstructure .............................................................. 51
    4.2.2 Oxidation Kinetics ................................................................................................................ 52
    4.2.3 Plan View Characterization of Oxide Scales (XRD and SEM) .......................................... 53
    4.2.4 TEM Microstructural and Chemical Analysis of Oxide Scales ........................................ 54
    4.2.4 Characterization of Internal Oxidation ................................................................................. 57
    4.2.5 Short-Term Oxidation Studies ............................................................................................... 58
  4.3 Discussion .................................................................................................................................... 59
### List of Figures

**Figure 1.1:** Schematic diagram of a solid oxide fuel cell showing how chemical energy is directly converted into electrical energy. Reproduced from [3]. ........................................ 15

**Figure 1.2:** A schematic diagram of a planar solid oxide fuel cell showing a “cross-flow” design where the fuel and air flow in different directions. Reproduced from [2].............................. 16
Figure 1.3: Backscattered electron images showing (a) Haynes 242; (b) Hastelloy S; and (c) Haynes 230 oxidized in moist air at 800° C for 300 hours. Note that Haynes 230 has the thinnest oxide scale under the same conditions. Reproduced from [14].

Figure 1.4: (a) Oxidation rate for some popular ferritic stainless steels plotted as weight gain (mg cm\(^{-2}\)) vs. time at 800° C reproduced from [6]. and (b) a similar plot for 441 HP also at 800° C following [6] using data from [17].

Figure 1.5: (a) ASR measurements at 800° C of ferritic stainless steel interconnect candidates performed at Julich and (b) ASR measurements at 800° C of stainless steel 441 with an without a protective coating performed at PNNL. Reproduced from [6,17].

Figure 1.6: (a) Strain vs. time for ferritic stainless steels at 700° C and a stress of 10 MPa and (b) the same plot at 800° C at the same stress. R indicates that rupture occurred. Reproduced from [8].

Figure 2.1: A schematic diagram of the transport processes through an SOFC interconnect oxide scale and coating. Reproduced from [24].

Figure 2.2: A schematic diagram of the magnetron sputtering process. Reproduced from [40].

Figure 2.3: A schematic diagram of an MOCVD apparatus. Reproduced from [36].

Figure 2.4: X-section SEM images of MCO coating (a) after reduction heat treatment in 2.75% H\(_2\)/Ar at 800 °C for 24 hrs.; (b) the same sample after oxidation in air at 800 °C for 100 hrs. Reproduced from [24].

Figure 2.5: A schematic diagram of a coated metal foil. X\(_c\) and X\(_f\) are coating thickness and oxide scale thickness respectively. Reproduced from [30].

Figure 4.1: Optical micrographs showing etched metallographic sections through coupons of the AR (a,b), HT1h (c,d) and HT4h (e,f) materials; (a), (c) and (e) are coupons before oxidation whereas (b), (d) and (f) are coupons oxidized at 800°C for 750 h.

Figure 4.2: Plot of parabolic weight gain (mg\(^2\)cm\(^{-4}\)) vs. exposure time for samples exposed in static air at 800 °C. The gravimetric rate constants (k\(_g\)) measured from the linear region between 250 h and 750 h were 4.82x10\(^{-8}\) mg\(^2\)cm\(^{-4}\), 2.82x10\(^{-8}\) mg\(^2\)cm\(^{-4}\) and 1.41x10\(^{-8}\)mg\(^2\)cm\(^{-4}\) for the AR, HT1h and HT4h samples, respectively.

Figure 4.3: Plan view BSE SEM images of the oxide scale surface for samples oxidized for 750 h at 800 °C: (a) AR, (b) HT1h and (c) HT4h.

Figure 4.4: XRD data obtained from the surface of samples oxidized for 750 h at 800 °C.
Figure 4.5: TEM data acquired from a FIB-cut cross section through the surface of an AR sample oxidized for 750 h at 800 °C: (a) BF TEM image; (b), (c) and (d) SADPs from regions 1, 2 and 3 in (a), respectively. The single crystal zone axis patterns in (c) and (e) correspond to a cubic spinel phase whereas the spotty rig pattern in (d) is consistent with the corundum structure of Cr$_2$O$_3$.

Figure 4.6: STEM data acquired from a FIB-cut cross section through the surface of an AR sample oxidized for 750 h at 800 °C. The BF image shows the region analyzed and the X-ray maps show the integrated intensities in 100 eV windows centered on the K\(\alpha_1\) energies for each element.

Figure 4.7: BF TEM images acquired from a FIB-cut cross section through the surface of samples oxidized for 750 h at 800 °C: (a) HT1h, (b) HT4h.

Figure 4.8: STEM data acquired from a FIB-cut cross section through the surface of an HT1h sample oxidized for 750 h at 800 °C: (a) BF image; (b) compositional profile obtained from spectra acquired at points along the horizontal line in (a).

Figure 4.9: STEM data acquired from a FIB-cut cross section through the surface of an HT4h sample oxidized for 750 h at 800 °C: (a) BF image; (b) compositional profile obtained from spectra acquired at points along the horizontal line in (a).

Figure 4.10: Bright field TEM image showing internal oxides in an HT4h sample oxidized for 750 h at 800 °C. The inset is an SADP taken from the oxide particle labeled “1”.

Figure 4.11: SE SEM images obtained from an AR sample oxidized for 5 h at 800 °C: (a) morphology of the oxide scale surface; (b) FIB-cut cross-section through the surface.

Figure 4.12: SEM data obtained from the surface of an AR sample oxidized for 5 h at 800 °C. The SE image shows the region analyzed and the X-ray maps show relative intensities proportional to the local composition of each element from quantitative analysis of EDXS data at each pixel.

Figure 4.13: SE SEM images obtained from an HT4h sample oxidized for 5 h at 800 °C: (a) morphology of the oxide scale surface; (b) FIB-cut cross-section through the surface.

Figure 4.14: SEM data obtained from the surface of an HT4h sample oxidized for 5 h at 800 °C. The SE image shows the region analyzed and the X-ray maps show relative intensities proportional to the local composition of each element from quantitative analysis of EDXS data at each pixel.
Figure 5.1: (a) BF STEM image acquired from a FIB-cut thin cross-section through the as-coated sample. (b) Compositional profile obtained from spectra acquired at points along the horizontal line in (a). (c)-(d) X-ray maps obtained from the area indicated by the dotted box in (a) using the integrated intensities in 100 eV windows centered on the K□ energies for: (c) Cr, (d) Co and (e) Mn. ................................................................. 97

Figure 5.2: STEM data acquired from a cross-section through the 250 h sample: (a) BF image; (b) compositional profile obtained from spectra acquired at points along the horizontal line in (a). ................................................................. 98

Figure 5.3: STEM data acquired from a cross-section through the 1000 h sample: (a) BF image; (b) compositional profile obtained from spectra acquired at points along the horizontal line in (a). ................................................................. 99

Figure 5.4: BF TEM acquired from a cross-section through the 1000 h sample. “SS” denotes pockets of subscale spinel observed between the alloy and chromia scale. ......................... 100

Figure 5.5: TEM data acquired from the following microstructural layers in a cross-section through the 1000 h sample: (a) and (b) SS pocket, (c) and (d) chromia scale, (e) and (f) RL. The SADPs in (b), (d) and (f) were obtained from the regions in the center of the areas shown in the BF TEM images (a), (c) and (e), respectively. ................................................................. 101

Figure 5.6: Overlay of the Cr compositional profiles from Figures 1(b), 2(b) and 3(b). In each case these are displaced laterally to give the alloy/chromia interface at 0.5µm for ease of comparison .................................................................................................................. 102

Figure 5.7: Schematic diagrams showing the development of microstructural layers and the senses of the associated diffusive fluxes during: (a) application of the MCO slurry; (b) reduction in Ar+H₂+H₂O; (c) re-oxidation in air; (d) the initial stages of long-term oxidation; (e) the later stages of long-term oxidation. Oxide phases are shaded grey, metallic phases are white and the black regions in (a) are pores. ......................................................................................... 103

Figure 6.1: Plot of parabolic weight gain (mg²cm⁻⁴) vs. exposure time for bare H230 exposed in static air at 800 °C. The gravimetric rate constant (kₜ) measured from the slope of the curve was 8.8x10⁻⁸ mg²cm⁻⁴s⁻¹ .............................................................................................................. 122

Figure 6.2: Plan view SEM images obtained from the surface of the scale formed on bare H230 after 1000 h oxidation in static air at 800 °C: (a) BSE image obtained with the electron beam
oriented perpendicular to the scale surface; and (b) SE image obtained with the sample tilted at 52° with respect to the beam. ................................................................. 123

**Figure 6.3:** STEM data acquired from a FIB-cut cross-section through the alloy/scale interface of a bare H230 sample oxidized for 1000 h at 800° C: (a) BF image; (b) compositional profile obtained from spectra acquired at points along the horizontal line in (a). 124

**Figure 6.4:** TEM data acquired from a FIB-cut cross section through the alloy/scale interface of a bare H230 sample oxidized for 1000 h at 800° C: (a) BF TEM image; (b) and (c) SADPs from regions 1 and 2 in (a), respectively. The spotty ring pattern in (b) is consistent with the corundum structure of Cr₂O₃ whereas the single crystal zone axis pattern in (c) corresponds to a cubic spinel phase. ................................................................. 125

**Figure 6.5:** SEM data obtained from a metallographic cross-section through the MCO-coated H230 sample after the reduction step of the reactive sintering process. The BSE image shows the region analyzed and the X-ray maps show the normalized relative intensities for the Co, Mn, Cr and Ni K lines, the W L line and the O K peaks after deconvolution for peak overlap. ............ 126

**Figure 6.6:** BSE SEM images obtained from metallographic cross-sections through MCO-coated H230: (a) after the reduction process and (b) after reduction and re-oxidation processes. ....... 126

**Figure 6.7:** STEM data acquired from a FIB-cut cross-section through the alloy/scale interface of an as-coated MCO/H230 sample (i.e. reduced and re-oxidized): (a) BF image; (b) compositional profile obtained from spectra acquired at points along the horizontal line in (a). ................................................................. 127

**Figure 6.8:** BF TEM image acquired from a FIB-cut cross-section through the alloy/scale interface of an as-coated MCO/H230 sample. ........................................................................................................ 128

**Figure 6.9:** STEM data acquired from a FIB-cut cross-section through the alloy/scale interface of an MCO-coated H230 sample oxidized for 1000 h at 800 °C. The DF STEM image shows the region analyzed and the X-ray maps show the normalized relative intensities for the Cr, Mn, Co and Ni K lines, the W L line and the O and Al K peaks. .................................................................................. 129

**Figure 6.10:** STEM data acquired from a FIB-cut cross section through the alloy/scale interface of an MCO-coated H230 sample oxidized for 1000 h at 800 °C: (a) BF image; (b) compositional profile obtained from spectra acquired at points along the horizontal line in (a). ....................... 130
**Figure 6.11**: TEM data acquired from a FIB-cut cross section through the alloy/scale interface of an MCO-coated H230 sample oxidized for 1000 h at 800 °C: (a) BF image; (b), (c) and (d) SADPs from regions 1, 2 and 3 in (a), respectively.

---

**List of Tables**

**Table 1.1**: Typical compositions of Ni-based superalloys used for SOFC interconnects [5, 14].
**Table 1.2**: CTE and resistivity values for some typical oxides formed on SOFC interconnect alloys [4].
**Table 1.3**: Compositions of some popular ferritic stainless steels that are being considered for SOFC interconnect applications [9].
**Table 1.4**: Compositions of additional ferritic stainless steels that are currently the most heavily researched [6, 13, 16].
**Table 2.1**: Thermal expansion and conductivity data for some typical SOFC interconnect coatings [22].
**Table 4.1**: Composition of Crofer 22 APU.
**Table 5.1**: Grain sizes measured from TEM cross-section samples for the chromia scale and the (Mn,Co,Cr,Fe)₃O₄ spinel RL.
**Table 6.1**: Composition of Haynes 230.
Chapter 1: Interconnect Alloys for Solid Oxide Fuel Cell

1.1 Introduction to Solid Oxide Fuel Cells (SOFCs)

SOFCs are a fuel cell technology that is designed to convert chemical energy directly into electrical energy. Theoretically they have very high efficiencies (> 50%) and can be used to convert various fuels (H₂, CO, methane, etc.) into electrical energy [1]. Recently the Solid State Energy Conversion Alliance (SECA) has set cost target and performance goals for SOFC stack development. Current cost targets are $400/ KW·h⁻¹. In addition, the stacks must meet a lifetime goal of 40,000 hours with performance degradation of less than 0.1% per thousand hours of operation [2]. Fuel cells are an attractive way to generate electrical energy because they contain no moving parts. Oxygen (or air) from the cathode side of the cell is dissociated into oxygen ions which diffuse through the electrolyte. Similarly, hydrogen molecules diffuse through the anode. The hydrogen molecules and oxygen ions react in the electrolyte to form water vapor and electrons. The electrons are pulled off the stack in the form of electricity. Figure 1.1 is a schematic diagram of the chemical reactions that occur within the fuel cell.

A typical fuel cell stack is made up of many different parts that when put together function as one unit. The cell itself is composed of 3 layers, namely the anode (typically Ni-YSZ cermet), the electrolyte (typically YSZ) and the cathode (La-Sr-Co-Fe-Mn containing oxides). Interconnects are conductive materials that connect adjacent cells while also separating the air in one repeat unit from the fuel in the next unit. Figure 1.2 below is an example of what a typical design of a planar solid oxide fuel cell might look like. It should be noted that some SOFC developers are also using a tubular design.
1.2 SOFC Interconnect Alloy Requirements

As of a few years ago, SOFCs were being run at temperatures around 1000° C. At these extreme temperatures all components of the fuel cell were by necessity made out of ceramic materials. The interconnect acts as a separator between the air on the cathode side of the cell and the hydrogen or fuel on the anode side of the neighboring repeat unit. The recent improvement of electrolyte materials has allowed operating temperatures of SOFCs to be decreased to 700-800° C. Thus, the traditional LaCrO$_3$ interconnect materials being used at 1000° C have now been replaced with metallic interconnects [3]. An extensive literature review on SOFC interconnects reveals that there are many requirements for a successful and durable interconnect material [5-12] and they include:

1) Gas tightness to prevent mixing of fuel and air
2) Good stability (oxidation and corrosion resistance), stable in air, fuel, water vapor and carbon containing environments.
3) High electrical conductivity of both the alloy and any oxidation products formed on the alloy during operation.
4) Thermal expansion coefficient match to the other fuel cell components, generally 10-13x10^{-6} K^{-1} [6].
5) High thermal conductivity to enable a uniform stack temperature.
6) Mechanical strength and durability at operating temperatures (good creep resistance)
7) Low cost to meet the requirements of $400 \text{ kW}^{-1}\text{hr}^{-1}$.
8) Chemical compatibility with other cell components (i.e. interconnect components can’t poison or degrade cell).
To date, there is no one material that can successfully meet all of these demands. For example, there are some Ni-base superalloys that meet the mechanical strength and oxidation resistance requirements, but they generally have CTE values higher than the required range. Many ferritic stainless steels which are currently the most popular choice for SOFC interconnects, meet the oxidation resistance requirements (with protective coatings), but do not have the mechanical strength (creep resistance) at elevated temperatures to hold up for 40,000 hours. Both of these shortfalls can possibly be worked around by alternative stack designs. However, the biggest drawback to metallic interconnects to date is that they are all chromia forming alloys. Chromia has been shown to be volatile at SOFC operating temperatures and is accentuated by the presence of water vapor [12, 13]. At low humidities non-conductive species can be formed and deposited on the cathode or electrolyte by the following reaction:

\[ \text{Cr}_2\text{O}_3 (s) + \frac{3}{2} \text{O}_2 (g) \rightarrow 2\text{CrO}_3(g) \ [13] \]

At higher humidities chromium hydroxides are formed:

\[ \text{Cr}_2\text{O}_3 (s) + \frac{3}{2} \text{O}_2 (g) + 2\text{H}_2\text{O} (g) \rightarrow 2\text{CrO}_2(\text{OH})_2 (g) \]

Both of the gaseous chromium containing species have been shown to re-deposit at the cathode or cathode/electrolyte interface and cause degradation of the cell voltage. This degradation is thought to be due to the fact that these chromium containing phases compete for triple phase boundary active sites were oxygen is reduced. By decreasing the number of oxygen molecules reduced, the chemical reaction is slowed and less voltage is produced. To date, there
is no replacement for chromia formers, as chromia is currently the only continuous oxide scale that is a semi-conductor at operating temperatures [9]. Chromia has a conductivity of $10^{-3}$-$10^{-2}$ S/cm at 800° C which is 5-6 orders of magnitude higher than the conductivity of alumina (Al$_2$O$_3$). Al$_2$O$_3$ or SiO$_2$ have better stability and about an order of magnitude slower oxidation rates than chromia formers, however their insulating properties have essentially taken them out of consideration for SOFC interconnect applications.

1.3 Typical SOFC Interconnect Alloys

While there are many classes of high temperature alloys that are considered for SOFC applications, some of them have major fallbacks and will not be discussed in detail in this review. For example, austenitic stainless steels which have an FCC structure have a CTE value of 18-20x10$^{-6}$ K$^{-1}$ between room temperature and 800°C. This is unfortunate since they have much higher mechanical strength than the ferritic stainless steels. Cr and Co-based alloys have been considered, but to date have not been shown to have properties as attractive as Ni-base superalloys or ferritic stainless steels. Neither Cr or Co-based alloys have the oxidation resistance required, and both are rather expensive to manufacture [5]. The next two sections will discuss Ni-base superalloys and ferritic stainless steels in more detail as these are the two general classes of material that are most promising for SOFC interconnect applications.

1.3.1 Ni-based Superalloys

To date, the most extensive review of SOFC interconnect alloys has been performed at Pacific Northwest National Laboratory (PNNL) by Yang and Stevenson (2003). They screened all of the major classes of high temperature alloys for oxidation resistance, area specific resistance (conductivity) and coefficient of thermal expansion. 17 total Ni-based superalloys were examined during their initial screening in 2003. In addition, the same group has performed
a more recent detailed study on three of the most promising Ni-based alloys (Haynes 230, Hastelloy S and Haynes 242). Ni-based alloys have a face-centered cubic (FCC) structure and generally contain carbide secondary phases that provide additional strength. In general, MC, M_{23}C_6, and M_6C are the most common with M typically being Mo, W, Ti, Nb, Ta or Cr [5].

1.3.1.1 Oxidation Resistance

Ni-based alloys are chromia formers as long as they contain greater than the critical percentage of Cr, which is about 20%. Thus, most Ni-based alloys for SOFC applications contain between 20-25 wt. % Cr. Al concentrations in these alloys are generally kept below 1.0 wt. % as too much Al can create unwanted internal Al₂O₃ formation which decreases the conductivity [14]. Similarly, Si content is also limited so as not to form continuous or internal SiO₂ phase. Table 1.1 shows a list of the Ni-based alloys that have been surveyed for their possible use as interconnect materials

In addition to their superior mechanical properties, Ni-based alloys also tend to have better oxidation resistance than ferritic stainless steels [9]. Out of all of the Ni-based alloys screened, Haynes 230 showed the slowest parabolic rate constant of 3.61x10^{-14} g^2 cm^{-4} s^{-1} which indicates the best oxidation resistance [5]. A detailed study of Haynes 230 and Hastelloy S showed that during oxidation Cr₂O₃ was the majority phase formed in addition to (Mn, Cr, Ni)₃O₄ spinel phases. Haynes 242 formed a two-phase oxidation scale consisting of an inner Cr₂O₃ scale and an outer NiO scale [14]. Figure 1.3 below shows representative micrographs of the three alloys oxidized in moist air (3% H₂O) at 800° C for 300 hours

1.3.1.2 Chemical Compatibility and Coefficient of Thermal Expansion (CTE)
While oxidation resistance and conductivities of Haynes 230 and Hastelloy S are more than acceptable for SOFC applications, chromia poisoning is still a concern as is the high CTE of Ni-based alloys which is mainly attributed to the FCC structure. BCC crystal structures such as ferritic stainless steels tend to have lower CTE values which match more closely with the cell materials.

Of the three Ni-based alloys studied in greater detail Haynes 230 had the highest CTE (14.9x10^{-6} K^{-1}) [14]. Literature shows that increasing Cr concentration in these alloys increases the CTE, while additions of Al, Mo, W and Ti decrease the CTE. Thus, it may be possible to decrease the CTE of Ni-based alloys to more closely match the 11-13x10^{-6} K^{-1} values necessary; however it must not be done at the expense of decreasing oxidation resistance.

1.3.1.3 Mechanical Properties

Ni-based alloys have much better mechanical properties than ferritic stainless steels at elevated temperatures. For example, Haynes 230 has a yield strength of 225 MPa and an ultimate tensile strength of 605 MPa at 760° C. Haynes 230 also has excellent rupture properties as it takes 140 MPa at 1,000 hours to cause rupture at 760° C [15]. As a comparison, stainless steel 441 which is a popular ferritic stainless steel for SOFC interconnects has a yield strength of 85 MPa and an ultimate tensile strength of 133 MPa at 760° C. In addition it has very poor rupture properties as it takes less than 7 MPa at 1,000 hours to cause rupture at 815° C [16]. It should also be noted that stainless steel 441 has a yield strength that is 2-3 times higher than typical ferritic stainless steels due to the formation of an Fe_{2}Nb laves phase [17].

Nickel based alloys will likely continue to be part of the solution toward solving the SOFC interconnect design problem, however their high CTE values and higher cost are the two biggest
factors limiting their current use. Currently, prices for Ni-based alloys are about four times higher than their stainless steel counterparts.

1.3.2 Ferritic Stainless Steels

The most popular choice of SOFC interconnect materials to date are the ferritic stainless steels. While Yang and Stevenson’s extensive review in 2003 covered a full range of alloys at the time, since their publication multiple alloys have been developed specifically for SOFC interconnects. The most popular to date is Crofer 22 APU which was jointly developed by Julich Institute of Energy (Germany) and ThyssenKrupp. In the U.S. the DOE is targeting stainless steel 441 alloy as the likely material for SOFC interconnects. Other specialty alloys such as IT-11, IT-14 (Plansee, powder metallurgy), Ebrite and ZMG232 (Hitachi Metals Ltd.) are also under consideration.

1.3.2.1 Coefficient of Thermal Expansion (CTE)

Ferritic stainless steels have a BCC microstructure which is why their CTE values typically range from about $11.5-14 \times 10^{-6} \text{ K}^{-1}$. This range is very close to the CTE values of the ceramic stack materials (e.g. YSZ). Cr is a BCC stabilizer and as a general rule the Cr concentration needs to be kept above approximately 13 wt. % as concentrations lower than this will lead to duplex (BCC + FCC) structures [5]. The CTE of ferritic stainless steels decreases with increasing Cr and Al content [17]. While in theory changing Cr and Al concentrations to change the overall CTE is possible, in practice these concentrations are set to maximize oxidation resistance. However, it has been shown that additions of other alloying elements such as Nb, Mo and W tend to decrease the CTE values as well, and can therefore be used to help tailor the values to closely match other SOFC components [9]. While the CTE of the
interconnect alloy is important, the oxidation products formed have their own unique CTE values which also need to be considered. Table 1.2 below shows the CTE and resistivity of common oxidation scales formed on SOFC alloys. Ideally, the CTE of the oxidized interconnect material should have a slightly higher CTE than the cathode and anode materials so the interconnects impart a compressive stress on the ceramic stack materials [9].

1.3.2.2 Oxidation Resistance and Conductivity

Similar to Ni-based alloys, the ferritic stainless steels being considered form Cr$_2$O$_3$ as an oxidation product. As a general rule, these ferritic stainless steels require approximately 18 wt. % Cr in order to form a continuous oxide scale [17]. If Cr concentrations are too high, sigma phases can form at the grain boundaries and embrittle the material. Additional alloying elements such as Mo can facilitate sigma phase formation, and therefore should be avoided. The sigma phase embrittlement has also been shown to cause a decrease in oxidation resistance due to Cr depletion [5]. Other minor alloying additions can have a substantial effect on both oxidation resistance and conductivity of the oxide scales formed. Table 1.3 is taken from Fergus’ review in 2005. Since then, additional alloys have surfaced as attractive candidates for interconnects; these additional alloys are given in Table 1.4.

While Cr concentration is extremely important for oxidation resistance of ferritic stainless steels, other minor alloying elements are also critical. For example, small Al and Si additions (< 1 wt.%) can slow down oxidation rates, but they do so at the cost of higher oxide scale resistivity [17]. Al concentrations of greater than 3 wt.% will eventually form a continuous Al$_2$O$_3$ insulating scale which is highly undesirable [5]. Si is a typical tramp element in ferritic stainless steels and in most cases is undesirable. For this reason, many manufacturers have had to use vacuum melting processes to eliminate such contaminants. Vacuum melting also
decarburizes the steel which minimizes C and N concentrations to less than 0.015 wt.%. These elements can be detrimental because they are austenite stabilizers. By minimizing the amount of interstitial C and N, more Cr can be dissolved into the matrix. These high purity, high Cr-containing alloys are often termed “super-ferritic”. E-brite is one example of a super-ferritic alloy which requires vacuum melting processing [5]. High purity alloys tend to minimize oxidation resistance [4]. For example, ITM (Plansee) alloys have been shown to have very good oxidation resistance due to their high purities. Small additions of Ti and Mn have the opposite effect compared to Al and Si as they tend to increase oxidation rate of the alloy, but have been shown to decrease the oxide scale resistivity [4,6]. The increase in oxidation rate with additions of Ti is due to the creation of cationic vacancies in Cr$_2$O$_3$ which is thought to cause faster Cr diffusion [4].

Recent studies on ferritics have shown that Nb and Si, which by themselves are often detrimental to oxidation rate (Nb) and oxide scale conductivity (Si), have a synergistic effect when present in the same alloy. Additions of 0.5 wt. % Nb can cause the precipitation of Fe$_2$Nb laves phase [8, 17]. It has been observed that tramp Si gets gettered by the Fe$_2$Nb laves phase at SOFC operating temperatures. Thus, higher cost vacuum melting processes can be avoided and the threat of forming an SiO$_2$ insulating scale is greatly reduced. The laves phase also tends to segregate to grain boundaries at elevated temperatures and it has been proposed that these phases can pin grain boundaries which results in increased creep resistance over typical ferritic stainless steels [17]. Currently, 441 HP (Allegheny Ludlam) is the best example of this two phase ferritic stainless steel. It has been shown by multiple groups that this combination of Nb and Si offers oxidation resistance and area specific resistance (ASR) that are comparable to Crofer 22 without the need for vacuum melting [8, 17].
Oxidation rate and oxide scale adhesion can also be altered by small additions of oxygen reactive elements such as Y, La, Ce, Nd and Zr. These elements tend to improve scale adhesion. They have also been shown to promote selective Cr oxidation in alloys that have lower Cr concentrations (<18 wt.%) [6]. For example, adding a small amount of Ce to an alloy containing 22 wt.% Cr has been shown to decrease the oxidation mass gain by fifty percent [1]. In practice, the most promising ferritic alloys for SOFC contain either La (Crofer 22, JS-3) or Y (IT-10, IT-11, IT-14). Figure 1.4 shows plots of weight gain vs. time at 800° C. Figure 1.4 (a) contains experimental data from Forschungszentrum Julich [6] which did not test stainless steel 441 HP. Figure 1.4 (b) was plotted following 1.4(a) from data collected at Pacific Northwest National Laboratories (PNNL) [17].

Ferritic stainless steels tend form different types of oxidation scales which is highly dependent on minor alloying additions. For example, Crofer 22 and ZMG-232 form a two layer oxide scale with an inner Cr_2O_3 scale and an outer (Mn,Cr)_3O_4 spinel phase. In addition small amounts of TiO_2 have been observed in the oxide scale, but this phase does not form a continuous layer as with the Cr_2O_3 and the spinel phase [6]. Similarly, 441 HP also forms a dual oxide scale with an inner chromia scale and an outer spinel phase [17]. IT alloys, which did not have Mn in their materials specification, were found to form Cr_2O_3 phase mixed with a small amount of (Mn,Cr)_3O_4 spinel and traces of Y_2Ti_2O_7. Ebrite is the only alloy in this group which forms a pure Cr_2O_3 scale with no other appreciable oxidation products [6].

While oxidation rate is an important factor in SOFC interconnect alloy selection, scale conductivity is even more critical. An alloy with very good oxidation resistance can only be used if the interconnect can maintain an area specific resistance (ASR) of 25-50 mΩ cm² over the 40,000 hour lifetime. Oxidation resistance and ASR are directly related. ASR values
increase following a parabolic rate law, much the same as weight gain [9]. Generally the oxide
scale dominates the ASR measurements as the non-oxidized base alloys have very low
resistivities (60-130x10^{-6} \, \Omega \, cm) [5]. However, the conductivity of oxidation products must
always be considered. For example, an alloy which forms a (Mn,Cr)₃O₄ spinel may have a
higher weight gain than an alloy forming a pure Cr₂O₃ scale, but could have a lower ASR due to
the higher conductivity of the spinel compared to chromia. Figure 1.5 shows typical ASR curves
for ferritic stainless steels. It should be noted that ASR data in 1.5 (a) was taken from Julich
while that in Figure 1.5(b) was measured at PNNL. Differences in measurement techniques
likely account for the different trends observed. The Julich measurements, Figure 1.5(a), were
performed with Pt paste with an applied current of 300 mA/cm² [6]. The PNNL measurements
were performed using La₀.₈Sr₀.₂MnO₃ and Pt wire contacts with a current density of 500 mA/cm²
[17]. It has since been shown that Pt paste reacts with the samples which reduces the overall
ASR values measured. Pt wire does not show this same effect. The need exists for a consistent
set of ASR measurements for all current alloy candidates.

Even if alloys can maintain an acceptably low ASR for 40,000 hours, scale adherence and
chemical compatibility are still key metrics that must be met. For example, stainless steel 441
has shown low oxide scale adherence after 900 hrs. at 800º C [17]. Thus, it is clear that in order
for this alloy to meet the requirements it will need to be modified by an oxygen active element
(Y, La, Ce, etc.) or coated.

While most interconnect alloys have been screened in air environments, it will become
exceedingly important to test SOFC interconnect materials in realistic operating environments.
Interconnects often act as the seal separating the air on the cathode side of the cell from the fuel
on the anode side of the cell. In order to cut cost, many interconnect designs are utilizing 0.1-1
mm thin foils [17]. This can severely change the oxidation resistance as there is a limited Cr reservoir. In addition, the dual atmosphere effect as first described by Yang may impose serious limitations to the implementation of metallic interconnects. In a dual atmosphere exposure test (H₂ on one side and air on the other), anomalous increase in oxidation is observed on the air side of the interconnect. Yang attributed this increase in oxidation rate to the diffusion of hydrogen through the alloy where it can locally change the transport properties of the chromia and an increased rate of Fe diffusion. [9]. Others have shown that water vapor causes an increase in oxidation rate of chromia forming ferritic stainless steels [12]. There are differing opinions as to whether or not chromia forming Ni-based alloys are similarly affected by water vapor and dual atmosphere exposure [6].

Other compatibility tests run in syngas (H₂, CO, CO₂, H₂S, water vapor) have shown that the oxidation products change in chemistry and morphology compared to oxidation tests run in air. For example, Crofer 22 forms a single oxide layer consisting of a mixture of Cr₂O₃ and Mn₁.₅Cr₁.₅O₄. This is in contrast to the dual layer oxide scale formed in air. In addition, whisker morphologies were observed on some of the alloys oxidized in syngas (both Ni-base and ferritics) [10]. These are important findings as syngas is one of the many fuels which may be used in SOFCs. This is one area where more testing clearly needs to be done to understand some of the fundamental mechanisms of gaseous reactions under SOFC operating conditions.

1.3.2.3 Chemical Compatibility

Much like Ni-based alloys that form continuous Cr₂O₃ scales, ferritic stainless steels one major drawback to date is their chemical poisoning effect on the fuel cell cathode. Initial testing
of un-coated ferritic stainless steels in fuel cells showed degradation rates as high as 25%/1000 hrs [17]. This is well above the target of 0.1%/1000 hrs.

To date, Julich has performed the most in-depth study on Cr vaporization. One of their major conclusions showed that alloys that formed (Mn,Cr)$_3$O$_4$ spinel outer layers had a 60-75% decrease in Cr vaporization compared to alloys forming pure Cr$_2$O$_3$. Crofer 22 and 441 fall into this category while alloys that form pure Cr$_2$O$_3$, such as E-brite, don’t fair as well [13]. While (Mn,Cr)$_3$O$_4$ spinel outer layers can slow down the Cr vaporization, they don’t eliminate it completely.

1.3.2.4 Mechanical Properties

As discussed in the Ni-based alloys section, one of the major drawbacks for ferritic stainless steels is their poor high temperature strength and creep resistance. Figures 1.6 (a) and (b) are strain vs. time curves for creep tests at 700º C and 800º C respectively.

Creep strength becomes increasingly important for interconnect designs that have thicknesses of 0.5 mm or less. It is clear from Figure 1.6 that additions of W cause slight improvements in solid solution strengthening and therefore creep resistance. Furthermore, the addition of Nb and Si to form laves Fe$_2$Nb laves phases also helps improve the creep properties. It is possible that the poor mechanical properties of ferritic stainless steels can be overcome by clever interconnect designs, however to date this is a severe limitation.

Clearly both ferritic stainless steels and Ni-based alloys both offer advantages and disadvantages for SOFC interconnect applications. Currently, no one alloy exists that meets all of the 8 requirements laid out in section 1.2. The implementation of top coatings (usually oxides) has increased the possibility of using metallic interconnects in solid oxide fuel cells. Short term tests show promising results, but long-term durability tests have not yet shown data to
suggest that there is an alloy/coating combination that can meet the 40,000 lifetime requirement while still maintaining low ASR and cell degradation.
Figure 1.1: Schematic diagram of a solid oxide fuel cell showing how chemical energy is directly converted into electrical energy. Reproduced from [3].
Figure 1.2: A schematic diagram of a planar solid oxide fuel cell showing a “cross-flow” design where the fuel and air flow in different directions. Reproduced from [2].

Figure 1.3: Backscattered electron images showing (a) Haynes 242; (b) Hastelloy S; and (c) Haynes 230 oxidized in moist air at 800° C for 300 hours. Note that Haynes 230 has the thinnest oxide scale under the same conditions. Reproduced from [14].
Figure 1.4 (a) Oxidation rate for some popular ferritic stainless steels plotted as weight gain (mg cm$^{-2}$) vs. time at 800° C reproduced from [6]. and (b) a similar plot for 441 HP also at 800° C following [6] using data from [17].
Figure 1.5 (a) ASR measurements at 800º C of ferritic stainless steel interconnect candidates performed at Julich and (b) ASR measurements at 800º C of stainless steel 441 with and without a protective coating performed at PNNL. Reproduced from [6,17].
Figure 1.6 (a) Strain vs. time for ferritic stainless steels at 700°C and a stress of 10 MPa and (b) the same plot at 800°C at the same stress. R indicates that rupture occurred. Reproduced from [8].
Table 1.1: Typical compositions of Ni-based superalloys used for SOFC interconnects.
Reproduced from [5, 14].

<table>
<thead>
<tr>
<th>Alloys&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
<th>Co</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Mo</th>
<th>W</th>
<th>Cb</th>
<th>Ti</th>
<th>Al</th>
<th>B</th>
<th>Others</th>
<th>UNS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hastelloy G-30</td>
<td>30</td>
<td>1 5</td>
<td>5 0</td>
<td>0 0</td>
<td>0.03</td>
<td>1.5</td>
<td>1.0</td>
<td>5.5</td>
<td>2.5</td>
<td>1.5</td>
<td>1.8</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>N96030</td>
</tr>
<tr>
<td>Inconel 690</td>
<td>61</td>
<td>0</td>
<td>5 0</td>
<td>0 0</td>
<td>0.02</td>
<td>0.2</td>
<td>0.2</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.2 Cu</td>
<td>N96690</td>
</tr>
<tr>
<td>Haynes HR-150</td>
<td>28</td>
<td>2</td>
<td>9 0</td>
<td>29</td>
<td>0.05</td>
<td>—</td>
<td>2.75</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>N12160</td>
<td></td>
</tr>
<tr>
<td>Nicrofer</td>
<td>25</td>
<td>0</td>
<td>9 5</td>
<td>0 0</td>
<td>0.20</td>
<td>0.1</td>
<td>0.5</td>
<td>0.5</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.15</td>
<td>2.1</td>
<td>—</td>
<td>N96025</td>
</tr>
<tr>
<td>6025HT-502CA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hastelloy</td>
<td>23</td>
<td>—</td>
<td>—</td>
<td>0.01&lt;sup&gt;e&lt;/sup&gt;</td>
<td>0.05&lt;sup&gt;e&lt;/sup&gt;</td>
<td>16.0</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1.6 Cu</td>
</tr>
<tr>
<td>C-2600</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inconel 601</td>
<td>60</td>
<td>3</td>
<td>2 0</td>
<td>14</td>
<td>—</td>
<td>0.05</td>
<td>0.5</td>
<td>0.2</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1.6</td>
<td>—</td>
<td>0.2 Cu</td>
<td>N96601</td>
</tr>
<tr>
<td>Inconel 939</td>
<td>22</td>
<td>5</td>
<td>2</td>
<td>0.5&lt;sup&gt;e&lt;/sup&gt;</td>
<td>10.0</td>
<td>0.15</td>
<td>0.2&lt;sup&gt;e&lt;/sup&gt;</td>
<td>0.2&lt;sup&gt;e&lt;/sup&gt;</td>
<td>2.2</td>
<td>—</td>
<td>3.7</td>
<td>2.0</td>
<td>0.014</td>
<td>1.1 Nb, 1.4 Ta</td>
<td></td>
</tr>
<tr>
<td>Haynes 230</td>
<td>22</td>
<td>0</td>
<td>5</td>
<td>0.10</td>
<td>0.5</td>
<td>0.4</td>
<td>2.0</td>
<td>14.0</td>
<td>—</td>
<td>—</td>
<td>0.3</td>
<td>0.005</td>
<td>0.02</td>
<td>La</td>
<td>N96230</td>
</tr>
<tr>
<td>Hastelloy X</td>
<td>22</td>
<td>0</td>
<td>5</td>
<td>1.5</td>
<td>0.10</td>
<td>1.0&lt;sup&gt;e&lt;/sup&gt;</td>
<td>1.0&lt;sup&gt;e&lt;/sup&gt;</td>
<td>9.0</td>
<td>5.6</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hastelloy C-22</td>
<td>51</td>
<td>6</td>
<td>1</td>
<td>1.5</td>
<td>2.5</td>
<td>0.01</td>
<td>1.0</td>
<td>0.1</td>
<td>13.5</td>
<td>4.0</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.3 V</td>
<td>N96222</td>
</tr>
<tr>
<td>Inconel 625</td>
<td>61</td>
<td>0</td>
<td>2</td>
<td>5.5</td>
<td>—</td>
<td>0.05</td>
<td>2.2</td>
<td>0.2</td>
<td>9.0</td>
<td>—</td>
<td>3.6</td>
<td>0.2</td>
<td>0.2</td>
<td>—</td>
<td>N96223</td>
</tr>
<tr>
<td>Inconel 622</td>
<td>21</td>
<td>0</td>
<td>4</td>
<td>2.5&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.015&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.5&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.08&lt;sup&gt;c&lt;/sup&gt;</td>
<td>13.5</td>
<td>—</td>
<td>—</td>
<td>0.5</td>
<td>0.3</td>
<td>—</td>
<td>0.35&lt;sup&gt;c&lt;/sup&gt; V</td>
<td>N96222</td>
</tr>
<tr>
<td>Inconel MA 754</td>
<td>78</td>
<td>3</td>
<td>—</td>
<td>20.0</td>
<td>—</td>
<td>0.05</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.5</td>
<td>0.3</td>
<td>—</td>
<td>0.6 Y&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>Nimonic 263</td>
<td>20</td>
<td>0</td>
<td>2.5</td>
<td>20.0</td>
<td>0.06</td>
<td>0.6b</td>
<td>0.4b</td>
<td>5.9</td>
<td>—</td>
<td>—</td>
<td>2.2</td>
<td>0.4</td>
<td>0.005</td>
<td>0.27 Cu</td>
<td>N97263</td>
</tr>
<tr>
<td>Inconel 625</td>
<td>19</td>
<td>5</td>
<td>2.5</td>
<td>25.5</td>
<td>0.07</td>
<td>0.5&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.5&lt;sup&gt;c&lt;/sup&gt;</td>
<td>4.3</td>
<td>—</td>
<td>—</td>
<td>3.0</td>
<td>1.4</td>
<td>0.005</td>
<td>0.25 Cu, 0.1 Cu&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>N97001</td>
</tr>
<tr>
<td>Pyronet 90</td>
<td>19</td>
<td>5</td>
<td>11</td>
<td>0.09</td>
<td>0.1&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.5&lt;sup&gt;c&lt;/sup&gt;</td>
<td>30</td>
<td>—</td>
<td>3.1</td>
<td>1.5</td>
<td>0.005</td>
<td>—</td>
<td>0.99 Zr</td>
<td>—</td>
<td>N97030</td>
</tr>
<tr>
<td>Haynes R-41</td>
<td>19</td>
<td>5</td>
<td>11</td>
<td>0.09</td>
<td>0.1&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.5&lt;sup&gt;c&lt;/sup&gt;</td>
<td>30</td>
<td>—</td>
<td>3.1</td>
<td>1.5</td>
<td>0.005</td>
<td>—</td>
<td>—</td>
<td>2097041</td>
<td></td>
</tr>
</tbody>
</table>

Table 1.2: CTE and resistivity values for some typical oxides formed on SOFC interconnect alloys. Reproduced from [4].

<table>
<thead>
<tr>
<th>Oxide</th>
<th>CTE (25–1000 °C) × 10&lt;sup&gt;-6&lt;/sup&gt; (°C&lt;sup&gt;−1&lt;/sup&gt;)</th>
<th>Electrical resistivity (Ω cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>9.6</td>
<td>100 at 800 °C</td>
</tr>
<tr>
<td>Mn&lt;sub&gt;1.5&lt;/sub&gt;Cr&lt;sub&gt;1.5&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>7.5</td>
<td>20 at 800 °C</td>
</tr>
<tr>
<td>NiO</td>
<td>14</td>
<td>5–7 at 900 °C</td>
</tr>
<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>7–8</td>
<td>100 at 900 °C</td>
</tr>
<tr>
<td>Mn&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>—</td>
<td>0.7–1 at 800 °C</td>
</tr>
</tbody>
</table>
Table 1.3: Compositions of some popular ferritic stainless steels that are being considered for SOFC interconnect applications. Reproduced from [9].

<table>
<thead>
<tr>
<th>Nominal compositions of iron-based alloys</th>
<th>Concentration (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy</td>
<td>Fe</td>
</tr>
<tr>
<td>Fe-10Cr</td>
<td>Bal</td>
</tr>
<tr>
<td>1.4724</td>
<td>Bal</td>
</tr>
<tr>
<td>SUS 430</td>
<td>Bal</td>
</tr>
<tr>
<td>Fe-17Cr-0.2Y</td>
<td>Bal</td>
</tr>
<tr>
<td>1.4016</td>
<td>Bal</td>
</tr>
<tr>
<td>Ferlotherm (1.4742)</td>
<td>Bal</td>
</tr>
<tr>
<td>Fe-18Cr-9W</td>
<td>Bal</td>
</tr>
<tr>
<td>Fe-20Cr-7W</td>
<td>Bal</td>
</tr>
<tr>
<td>Fe-20Cr</td>
<td>Bal</td>
</tr>
<tr>
<td>ZMG 252</td>
<td>Bal</td>
</tr>
<tr>
<td>AL 453</td>
<td>Bal</td>
</tr>
<tr>
<td>Fe22CrMoTiY</td>
<td>Bal</td>
</tr>
<tr>
<td>1.4763(446)</td>
<td>Bal</td>
</tr>
<tr>
<td>FeCrMo(LaTi)</td>
<td>Bal</td>
</tr>
<tr>
<td>Fe-Cr-Mn</td>
<td>Bal</td>
</tr>
<tr>
<td>Fe-25Cr-DIN 50049</td>
<td>Bal</td>
</tr>
<tr>
<td>Fe-25Cr-0.1Y-2.5Ti</td>
<td>Bal</td>
</tr>
<tr>
<td>Fe-25Cr-0.2Y-1.6Mn</td>
<td>Bal</td>
</tr>
<tr>
<td>Fe-25Cr-0.4La</td>
<td>Bal</td>
</tr>
<tr>
<td>Fe-25Cr-0.3Zr</td>
<td>Bal</td>
</tr>
<tr>
<td>Fe26CrTiY</td>
<td>Bal</td>
</tr>
<tr>
<td>Fe26CrTiYNbY</td>
<td>Bal</td>
</tr>
<tr>
<td>Fe26CrMoTiY</td>
<td>Bal</td>
</tr>
<tr>
<td>E-Brite</td>
<td>Bal</td>
</tr>
<tr>
<td>AL-29-4C</td>
<td>Bal</td>
</tr>
<tr>
<td>Fe-30Cr</td>
<td>Bal</td>
</tr>
</tbody>
</table>

Symbol "?" indicates element is present, but concentration is not specified.

Table 1.4: Compositions of additional ferritic stainless steels that are currently the most heavily researched. Reproduced from [6, 13, 16].

<table>
<thead>
<tr>
<th>Concentration Wt.%</th>
<th>Alloy</th>
<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
<th>Mn</th>
<th>Nb</th>
<th>Mo</th>
<th>W</th>
<th>Si</th>
<th>Al</th>
<th>Ti</th>
<th>Y</th>
<th>Zr</th>
<th>La</th>
<th>Ref. #</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crofer 22 APU</td>
<td>Bal.</td>
<td>22.78</td>
<td>0.02</td>
<td>0.4</td>
<td>n.a.</td>
<td>n.a.</td>
<td></td>
<td></td>
<td></td>
<td>0.02</td>
<td>0.006</td>
<td>0.07</td>
<td></td>
<td>0.066</td>
<td>0.13</td>
</tr>
<tr>
<td>JS-3</td>
<td>Bal.</td>
<td>22.77</td>
<td>0.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.02</td>
<td>13</td>
</tr>
<tr>
<td>FT-14</td>
<td>Bal.</td>
<td>26.3</td>
<td>0.17 n.a.</td>
<td>0.02</td>
<td>n.a.</td>
<td>n.a.</td>
<td></td>
<td></td>
<td></td>
<td>0.02</td>
<td>0.002</td>
<td>n.a.</td>
<td>0.06</td>
<td>-</td>
<td>0.13</td>
</tr>
<tr>
<td>FT-11</td>
<td>Bal.</td>
<td>26.4</td>
<td>0.3</td>
<td>n.a.</td>
<td>0.01</td>
<td>0.02</td>
<td>n.a.</td>
<td></td>
<td></td>
<td></td>
<td>0.08</td>
<td>-</td>
<td>0.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FT-10</td>
<td>Bal.</td>
<td>25.5</td>
<td>0.3</td>
<td>n.a.</td>
<td>0.02</td>
<td>n.a.</td>
<td>0.07</td>
<td></td>
<td></td>
<td></td>
<td>0.07</td>
<td>-</td>
<td>13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AL 441 HP</td>
<td>Bal.</td>
<td>18</td>
<td>0.3</td>
<td>0.35</td>
<td>0.5</td>
<td></td>
<td>0.34</td>
<td>0.08</td>
<td>0.22</td>
<td>0.04</td>
<td>0.07</td>
<td>0.08</td>
<td></td>
<td>16</td>
<td></td>
</tr>
</tbody>
</table>
2. Coatings for SOFC Interconnects

2.1. Introduction to Coatings

As briefly touched upon in the previous section, SOFC cathodes are especially susceptible to volatile Cr (VI) compounds. Rapid poisoning of active triple phase boundaries between air, electrolyte and cathode materials can occur in the presence of CrO₃ and CrO₂(OH)₂[20]. Calculations have shown that Cr₂(OH)₂ partial pressures under anode operating conditions are 7 orders of magnitude lower than that of the cathode, thus Cr poisoning is not thought to be an issue for the anode[21]. Testing done at Julich Research Center (Germany) on uncoated Crofer 22 showed degradation rates of 21%/1000 hours. In order to make SOFCs competitive with other technologies, degradation rates must fall below 2%/1000 hours for short-term mobile applications [22] and 0.1%/1000 hours for longer term stationary applications[23]. Specialty SOFC interconnect alloys such as Crofer 22 which form a protective outer (Mn,Cr)₃O₄ spinel have only been shown to decrease Cr volatility by a factor of 2-3 compared to Cr₂O₃ at 850 °C[24]. In addition to limiting Cr volatility and Cr diffusion, coatings can also retard oxidation, therefore reducing areas specific resistance (ASR) compared to uncoated alloys[25].

It has shown that chromia forming alloys form their scales by diffusion of Cr cations outward and O anions inward. Thus, good SOFC interconnect coatings will act as a diffusion barrier for Cr while also having an acceptably low O ion conductivity[26]. Figure 2.1 below is a schematic diagram of a coated chromia forming alloy. Note that in order for metal ions to diffuse through the chromia scale, the chromium atoms must first be reduced. The ions can then subsequently transport through the scale together with the electrons to combine with oxygen ions at the surface and create Cr₂O₃. This complex process will be discussed in further detail in a later section.
Coatings must also maintain a sufficient electrical conductivity as one of the interconnect functions is to pull power off of the cell. In addition, it is very important to maintain zero open porosity, such that there are no short circuit paths for oxygen diffusion to the interconnect[27]. Predicting the lifetime of coated interconnects remains one of the most difficult tasks to date. While the systems must last a minimum of 40,000 hours, testing for this period of time is impractical. Some groups have taken on accelerated testing by running at increased temperatures (e.g. 900 °C), but have reported that kinetics and mechanisms often change [28]. Other groups have attempted to combine oxide growth kinetic data with mechanical adhesion tests to project lifetimes from a mechanical integrity standpoint. PNNL is one group that has done this using microhardness indentation with gradually increasing loads to measure coating adhesion. By combining adhesion data with oxidation kinetics, they have predicted that uncoated Crofer 22 will fail at a coating thickness of 11.2 µm, which corresponds to 4750 hours of operation at 800 °C. A Mn\textsubscript{1.5}Co\textsubscript{1.5}O\textsubscript{4} (MCO) spinel coated Crofer test which would currently be considered by most as the best ferritic stainless steel combined with the best coating shows a predicted lifetime of 15,500 hours. It should be noted that coatings reduce the critical scale thickness, such that a 4.2 µm thick chromia scale beneath the MCO coating would cause mechanical failure [29]. Still others have modeled stresses and determined that combined chromia scale and coating thicknesses must be less than 10 µm for sufficient mechanical stability [30]. In practice, it depends on the thermal expansion mismatch between the coating/oxide scale and the other cell components.
In the sections that follow, an overview of SOFC interconnect coatings will be discussed. Section 2.2 will discuss different types of interconnect coatings and their effectiveness followed by a brief discussion of coating application methods in Section 2.3. Section 2.4 is a rather detailed analysis of oxidation kinetics, including factors affecting conductivity and diffusivity. Section 2.5 will discuss specific coating/substrate interactions in more detail and finally Section 2.6 will give a brief overview of how all of the factors at play can affect area specific resistance (ASR). Section 2.6 is of particular importance since ASR is a good indicator of how a material would perform in actual SOFC operating conditions.

2.2 Types of SOFC Interconnect Coatings

SOFC interconnect coatings to date fall into three main categories: spinel oxide coatings, perovskite coatings and reactive element oxide coatings. To date none of the coating/alloy combinations trend toward meeting the stringent 40,000 hour lifetime, but spinels appear to be the most attractive at present. The following is a summary of the current literature on each of the three general classes of coating. Table 2.1 below is a partial list of common SOFC coatings studied to date along with coefficient of thermal expansion (CTE) values and thermal conductivity values. This is not a complete list, nor does it take into consideration Cr volatility resistance.

2.2.1 Spinel Coatings

Spinels are a class of mineral having a cubic crystal structure with the chemical formula: \( \text{AB}_2\text{O}_4 \). In a model spinel structure the A-sites are divalent (2+) and the B-sites are trivalent (3+), however divalent, trivalent and quadrivalent cations may occupy either A or B sites. A typical spinel structure consists of an FCC packing of oxygen anions with divalent cations occupying 1/8 of the tetrahedral sites and trivalent cations occupying up to half of the octahedral
While different coating application methods will be discussed in more detail in Section 2.3, it should be noted that spinel coatings are either deposited as the oxide or as a metallic layer which then oxidizes into a stable spinel phase. To date the most popular spinels contain Mn and Co. $\text{Mn}_{1+\delta}\text{Co}_{2-\delta}\text{O}_4$ (MCO) spinels have been the most extensively studied. It has been reported that for $0.3<\delta<0.9$ the MCO spinels have a mixed cubic and tetragonal crystal structure. For $\delta<0.3$ the stable crystal structure is cubic and for $\delta>0.9$ the tetragonal crystal structure is stable. Yang et.al. have extensively studied the $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$ composition, as this appeared to be the most promising in their initial screening of different compositions. While this specific composition is not given in Table 2.1, it was chosen due to the fact that it has a conductivity of 60 S cm$^{-1}$ at 800 °C. This is approximately 3 orders of magnitude higher than the electrical conductivity reported for $\text{MnCr}_2\text{O}_4$ which forms as an oxide scale on Crofer 22 [25].

Cyclic oxidation studies on bare and MCO coated stainless steel 430 showed good coating adherence during cycling and the parabolic rate constant for oxidation of the MCO coated sample was reported to be $1.95\times10^{-15}\text{g}^2\text{cm}^{-4}\text{s}^{-1}$ at 750 °C. This is an improvement of almost 2 orders of magnitude in oxidation rate compared to the bare 430 tested in the same manner [32]. PNNL has shown that MCO spinel coatings successfully minimize contact resistance and lower Cr volatility [24]. However, ASR tests on MCO coated Crofer 22 showed that the adhesion of these coatings may be an issue for long-term applications. For this reason Ce was added to the coating as a reactive element in order to increase oxide scale and coating adherence to the metal substrate. A composition of $\text{Ce}_{0.5}\text{Mn}_{1.475}\text{Co}_{1.475}\text{O}_4$ was used and results to date have looked promising [26]. To the author’s knowledge, these are the longest tested coatings to date in ASR tests had been reported out to about 10,000 hours as of January, 2010.
Other groups have also reported success with doping the MCO spinel with Fe. A study done at Julich Forschungszentrum showed drastic reductions in contact resistance in Crofer 22 and F18TNb coated with a MnCo$_{1.9}$Fe$_{0.1}$O$_4$ spinel, but little effect on Ebrite and ITM alloys. The authors note that the main difference is that Crofer 22 and F18TNb alloys both contain Mn, while Ebrite and ITM alloys do not [33]. Interactions between coatings and alloys are extremely important and as such, Section 2.5 is devoted entirely to this topic.

2.2.2 Perovskite Coatings

Perovskites are classified by their ABO$_3$ chemical formulas. The undistorted perovskite structure is cubic, with a unit cell were A cations occupy the corners of the cube, B cations occupy the body center position and oxygen anions sit at the face centers [31]. In reality perovskite structures can be cubic, orthorhombic, tetragonal or trigonal. These oxide coatings are attractive because many of them are electrically conductive, have a good CTE match to other cell components and can be used to incorporate reactive elements into the system. While one group showed that La$_{0.65}$Sr$_{0.3}$MnO$_3$ (LSM) and La$_{0.6}$Sr$_{0.4}$Co$_{0.8}$Fe$_{0.2}$O$_3$ (LSCF) coatings reduced Cr volatility by a factor of 40 [21], most others have shown that these coatings do not perform well as Cr barrier coatings due to rapid diffusion of Cr through the coatings [22,24,31]. Other common compositions studied include La$_{0.8}$Sr$_{0.2}$CrO$_3$ (LSC), LaCrO$_3$ (LC) and Ti-doped LaMnO$_3$ [30,34,35]. One can alter ionic conductivity by doping these perovskites, however it has been shown to date that the high ionic conductivities of most perovskites makes them impractical for slowing down Cr cation and O anion diffusion. These materials are commonly used as SOFC cathode materials due to their mixed ionic and electronic conductivity.
2.2.3 Reactive Element Oxide Coatings

Reactive element oxides have many beneficial effects which will be discussed in further detail in later sections, however the few papers available in the literature show that they are not likely candidates for SOFC coatings by themselves. These coatings are generally thin (<1 µm) and while they can act to slow down outward Cr diffusion and increase chromia scale adhesion, they have not been shown to block volatile Cr species [31]. The most extensive study to date examined La$_2$O$_3$, Nd$_2$O$_3$ and Y$_2$O$_3$ coatings on Crofer 22, AL 453 and Haynes 230. Out of the three coatings evaluated, only the La$_2$O$_3$ reduced the oxidation rate of H230. This indicates that the Nd$_2$O$_3$ and Y$_2$O$_3$ coatings had little if any effect on slowing oxidation rates [36]. While reactive element oxides may play a role in SOFC coatings, it will likely be as a minor element such as that used in MCO spinels to increase scale adhesion. It should be noted that the reactive elements can be added to the system by alloying the metal substrate, surface treatment of the metal or by incorporating the reactive elements into the interconnect coating.

2.3 Methods of Coating Application

One of the difficulties in evaluating and comparing the different types of coatings discussed in the previous section is the large number of coating application processes used to deposit coatings. To date, there have been many techniques used, but there are four specific coating techniques that appear most frequently: Magnetron sputtering, electroplating, metal organic chemical vapor deposition (MOCVD) and slurry processing. The following sections will be devoted to these coating techniques. In addition, it should be noted that additional coating techniques such as large area filtered arc deposition (LAFAD) [21,24], vacuum plasma spraying [21], pack cementation [37] and pulsed laser deposition (PLD) [38] have also been reported in
the literature. These coating methods will not be discussed in detail, but may still be viable techniques.

2.3.1 Magnetron Sputtering

Multiple groups have reported the use of either DC or rf-Magnetron sputtering to deposit oxidation resistant interconnect coatings. Magnetron sputtering is a form of physical vapor deposition (PVD). The technique involves placing the samples to be coated into a vacuum chamber. The desired coating material is placed in the apparatus as the target and a magnet is placed behind the target to collect unwanted electrons from the plasma. The magnetic fields used are on the order of hundreds of gauss, thus they can affect the electrons in the plasma, but not the ions [39]. Argon gas is bled into the chamber and a plasma is generated by applying an electric field. The argon ions strike the target material and energetically knock off ions and molecules from the target surface. Generally a negatively charged bias is applied to the target in order to enhance sputtering of the target surface. The vapor formed is then deposited on the substrate to form a coating. 2.2 below is a schematic diagram of a typical DC Magnetron setup.

Radio frequency magnetron sputtering is a similar setup, which is used to sputter non-conductive target materials. SOFC interconnect coatings have been applied using DC and rf magnetron sputtering to produce perovskite and spinel coatings. Typically the coatings formed are thin (0.3-1 µm), but can be thicker if longer deposition times are used. La_{0.67}Sr_{0.33}O_3 (LSM) coatings were prepared by DC magnetron sputtering by two independent groups. Both successfully deposited thin films using this technique, but after deposition the coatings were amorphous. Upon heating to crystallize the coating, the coating formed mud cracks and in some cases de-laminated from the substrate. One group attributes this to differences in thermal expansion between the coating and the substrate [41] and the other postulates that this may be
due to volume changes that occur during the crystallization process [40]. Another group studied LaCrO$_3$ coatings deposited by magnetron sputtering. Once again the as-deposited coatings were amorphous and needed to be heat-treated to form a crystalline coating. While no de-lamination was reported, the authors noted that the samples which were crystallized in air were much more porous than those crystallized in a reducing atmosphere [35].

Magnetron sputtered metallic Mn$_{50}$Co$_{50}$ coatings were used as a precursor for forming an MCO spinel phase. Pure metals offer advantages because they have much higher sputter yields than their oxide counterparts; however the authors report that a 1 µm thick metallic coating still takes over 1.5 hours to deposit [42]. The slow deposition rate, high cost of equipment and difficulty in scalability severely limits this as a coating approach for inexpensive manufacturing, however for research purposes this appears to be a serviceable technique.

2.3.2 Electroplating

Electroplating is a simple process in which an electrochemical cell is connected through an electrolyte solution. The electrolyte generally contains salts of the metal species to be plated. The anode can either be a pure metal which is the same as the metal in the electrolyte, or a noble metal such as platinum. The part to be plated is the cathode. When a DC current is applied, metal at the anode is oxidized and goes into solution. The applied current accelerates the positive metal ions to the negatively charged cathode. This coating approach has been used extensively to deposit SOFC interconnect coatings. Electroplating is limited to conductive materials, as such metals are the most commonly plated materials.

Since many transition metals naturally form spinels as an oxidation product, numerous groups have produced coatings via electroplating metals followed by oxidizing the coatings in air. MCO spinels produced with this process were dense and continuous after oxidizing the
electroplated alloy coating [43]. Similar successes were reported for the formation of NiFe$_2$O$_4$ spinel coatings [44]. One benefit of plating is that it is a very versatile process, for example it is possible to incorporate non-conductive second phase particles in a metallic matrix. This was demonstrated by Shaigan et. al. who produced a dense coating of LaCrO$_3$ in a metallic Co matrix [45]. Overall electroplating followed by oxidation appears to be an attractive method for SOFC interconnect coatings. The process is simple, inexpensive and is already used in numerous manufacturing processes.

### 2.3.3 Metal-Organic Chemical Vapor Deposition (MOCVD)

Metal organic chemical vapor deposition (MOCVD) is a coating process commonly used to produce thin compound semiconductors for the electronics industry. The process involves using a metal alkyl or metal hydride precursor that is heated to the vapor phase. A sophisticated gas-switching manifold is used to introduce the vapors into a cold wall reactor. In many cases hydrogen is used as a carrier gas. This process is somewhat complex, but with optimization it has been shown to give reproducible coating thickness and chemistry to +/- 1% [46]. To date, this coating technique has been reported in the literature by Fontana et. al for depositing thin coatings of reactive element oxides such as La$_2$O$_3$, Nd$_2$O$_3$ and Y$_2$O$_3$ [20,23,36,47]. MOCVD was used to deposit 100-200 nm thick coatings on numerous alloys including Crofer 22, Haynes 230 and AL 453. The authors report nanocrystalline coatings in the as-deposited state. A schematic diagram of the coating process is given in Figure 2.3. MOCVD is a technique that will likely aid in preparing thin, homogeneous coatings for fundamental studies, but it is not likely to be a scalable low-cost manufacturing process.
2.3.4 Slurry Coating Processes

Slurry processing offers a low cost, highly manufacturable method of depositing SOFC interconnect coatings. This process has been successfully demonstrated by numerous groups, and is quite attractive due to the possibility of scale-up using screen painting, printing, spraying or dip coating processes. Slurry coating is a multi-step process that generally starts with the production of a fine, chemically homogeneous ceramic powder. PNNL reported using both solid-state reaction and glycine-nitrate combustion techniques to produce MCO spinel powder precursors. It was found that the glycine-nitrate combustion synthesis resulted in more homogeneous powders that were smaller in diameter than those formed through solid-state reaction processes [25]. The glycine-nitrate process uses nitrate precursor solutions (i.e. Mn(NO$_3$)$_3$ and Co(NO$_3$)$_3$) which are mixed with glycine and heated until they combust. The reaction product is then calcined in air.

A slurry suspension is created by adding a binder and the slurry is then typically ball milled to form the final slurry which is then applied to the interconnect surface by painting, spraying, dipping or screen-printing. Montero et. al. (Julich) incorporated a two-step reactive sintering process consisting of a reducing treatment in Ar/3% H$_2$O/4% H$_2$ at 800 °C for 2 hours followed by oxidation in air at the same temperature for 10 hours [33]. PNNL has reported similar reactive sintering processes for MCO spinel coatings, of which the reduction step results in the formation of Co metal and MnO. The oxidation step causes these products to react along with oxygen to form the final (Mn,Co)$_3$O$_4$ spinel. Figure 2.4 below shows x-section SEM images of an MCO coating after each phase of the reactive sintering process [24].

While reactive sintering aids in forming a relatively dense coating, there are possible negative effects that have been recently reported by the current author. It has been shown that in the case
of Haynes 230, exposing the alloy to the reduction treatment results in a debit in oxidation resistance [48]. This is a phenomenon that must be further understood in order to optimize the interconnect alloy and coating systems. Overall, slurry coating is an attractive and flexible coating process, however further improvements in processing to reduce internal porosity and scale up for manufacturing are still required.

2.4 Kinetics and Transport in Coated Alloy Systems

2.4.1 Oxidation Kinetics of Chromia Formers

Cr₂O₃ is the only thermodynamically stable chromium oxide phase known to exist in the solid state. Cr₂O₃ (corundum) has a crystal structure similar to that found in Al₂O₃, wherein oxygen anions occupy a close-packed hexagonal structure and Cr cations occupy 2/3 of the octahedral sites [49]. Oxidation of metallic Cr species is a thermodynamically driven process; ionic transport of species occurs due to the oxygen potential difference between the scale/gas interface and the scale/alloy interface [50]. Numerous studies have been performed on pure chromia or chromia forming alloys, but extremely slow diffusion of O²⁻ and Cr³⁺ within the Cr₂O₃ scale currently limit a more detailed understanding. To date, there has been conflicting diffusion data for Cr cations and O anions in Cr₂O₃. It is well known that defects in the oxide scale play a large role in determining transport through the scale. Fundamental studies by Kofstad show that grain boundary (GB) diffusion in chromia can dominate over lattice diffusion. Diffusion along grain boundaries is thought to be most important at lower temperatures due to the lower activation energy of GB diffusion compared to lattice diffusion. This is thought to be due to both the very slow self-diffusion coefficients of Cr and O in Cr₂O₃ and the correspondingly small number of point defects in the chromia scale. The lattice self-diffusion coefficients of Cr and O in single crystals of Cr₂O₃ have both been measured to be ≈ 10⁻¹⁷ cm²/s
at elevated temperatures (1100-1300 °C). Polycrystalline samples show diffusion rates that are a few orders of magnitude higher than single crystals, which speak to the importance of GB transport in Cr₂O₃ [51].

It is well known that the fastest diffusing species in a counter diffusion process is the rate-limiting step. It was widely thought that Cr cations diffused faster through the Cr₂O₃ scale than O anions. This was reported by England and Virkar for Ni-base superalloy systems [52]. Horita et. al. measured diffusion coefficients of O²⁻ in Fe-Cr alloy systems that were two orders of magnitude higher than the growth rate of the oxide scale. This again is attributed to oxygen diffusion along grain boundaries. A detailed SIMS analysis was used to trace a stable ¹⁸O isotope. It was determined that while the oxygen diffusion was fast through the bulk of the Cr₂O₃ (D₀=5.5x10⁻¹² at 800°C), it was rather sluggish close to the alloy/Cr₂O₃ interface. Thus, oxidation rate was presumed to be controlled by the Cr cation diffusion close to the alloy/Cr₂O₃ interface [53]. Others have proposed a two-way transport mechanism of Cr cation lattice diffusion outward and O anion diffusion inward; this is a reasonable explanation, especially when localized blisters and nodules are present. The same author also notes that surface preparation drastically affects the stresses that build up during oxide scale growth and can drastically change the oxidation rate. In addition, rapidly forming a chromia scale may be undesirable due to the resulting small grain size and increased GB area [49].

Traditionally, oxidation kinetics of most alloys tend to follow a parabolic relationship and chromia formers such as Crofer 22 and H230 follow Wagner’s theory. Oxidation rates of different alloys or alloy/coating systems tend to be expressed with either the parabolic rate constant, kₚ (cm²/s) or kₚ (mg²/cm⁴·s). From Wagner’s simplified theory for the oxidation of metals, a parabolic rate constant for Cr₂O₃ can be expressed as follows:
\[ kp = \frac{CO}{2b} \int_{p_{O_2}}^{p'_{O_2}} \left( \frac{3}{2} D_{Cr} + D_{O} \right) d \ln P_{O_2} \] [53].

Where \( D_{Cr} \) and \( D_{O} \) are self-diffusion coefficients in \( Cr_2O_3 \), \( C_O \) and \( b \) are constants, \( p'_{O_2} \) and \( p''_{O_2} \) are oxygen partial pressures of the \( Cr_2O_3/\)atmosphere and the alloy/\( Cr_2O_3 \) respectively. Again, note that based on this equation the fastest diffusing ion controls the oxidation rate, however oxygen partial pressure difference is also an important factor [53]. One must then consider the mobility of the ionic species diffusing, which is related to ionic conductivity by the Nernst-Einstein relationship:

\[ \sigma_i = \frac{z_i^2 e^2 c_i D_i}{kT} \] [48].

Where \( \sigma_i \) is the ionic conductivity of the diffusing species, \( z_i \) is the net charge of the ion, \( c_i \) is the ion concentration (atoms/volume) or concentration of mobile defects, \( k \) is Boltzmann’s constant and \( T \) is temperature. From this relationship it can be clearly seen that as ionic conductivity increases, so does the diffusion coefficient of the ionic species. Thus, ideal coating systems for SOFC applications will have low \( Cr^{3+} \) and \( O^{2-} \) conductivity, but still maintain an acceptable electronic conductivity.

Many times the oxidation rate constant \( k_g \) is used to express the kinetics in terms of weight gain:

\[ \left( \frac{w}{A} \right)^2 = k_g t \] [52].

Where \( w \) is the weight gain, \( A \) is the surface area of the sample and \( t \) is the time exposed to oxidation conditions. This constant is far more convenient for experimentally comparing oxidation of different coated alloy systems.
In general, Ni-Cr superalloys tend to have more sluggish oxidation kinetics compared to their Fe-Cr counterparts. England and Virkar extensively studied the oxidation kinetics of four Ni-base superalloys (Inconel 625, 718, Hastelloy X, Haynes 230) and reported that H230 had the slowest oxidation kinetics at 800 °C ($k_g=1.29 \times 10^{-9}$ mg$^2$/cm$^4$s) [52]. In comparison, Yang et. al. reported oxidation kinetics of bare Crofer 22 at 800 °C to be faster than that of H230 ($k_g =8.00 \times 10^{-8}$ mg$^2$/cm$^4$s) [34]. While it is still not generally discussed in the literature, the difference in kinetics between Ni-base and Fe-base alloys is presumably due to differences Cr diffusion through the bulk lattice of the alloy. Impurities, morphology and density of the Cr$_2$O$_3$ scale also are likely to strongly influence the overall oxidation kinetics.

### 2.4.2 Oxidation Kinetics of Coated Alloy Systems

Numerous theories have been proposed to attempt to describe the oxidation kinetics and mechanisms of coated systems. Huang et. al. [54] and Patterkine et. al [30] separately proposed models which take into account the properties of both the thermally grown Cr$_2$O$_3$ scale and the coating. Figure 2.5 is a schematic diagram adopted from Patterkine et. al. of a simple coated alloy system.

Both the coating and the oxide scale have their own individual rate constants, termed $k_c$ and $k_f$ respectively and the kinetics of oxidation of a coated alloy system are given by the following equation:

$$k_c x_f^2 + 2k_f x_c x_f = k_f x_f t$$  \hspace{0.5cm} (eqn. 1)

Where $t$ is the oxidation time, and the rest of the parameters are defined above. Furthermore, each rate constant can be expressed in terms of its ionic and electronic conductivities as follows:
\[ k_f = \frac{EV_M}{2F} \left( \frac{\sigma_i f \sigma_e f}{\sigma_i f + \sigma_e f} \right) \] (eqn. 2)

Where \( E \) is the nernst voltage related to the oxide scale formation, \( F \) is the Faraday constant, \( V_M \) is the molar volume of the oxide scale and \( \sigma_i f \) and \( \sigma_e f \) are the ionic and electronic conductivities of the scale. The same relation can also be written for the rate constant of the coating:

\[ k_c = \frac{EV_M}{2F} \left( \frac{\sigma_i c \sigma_e c}{\sigma_i c + \sigma_e c} \right) \] (eqn. 3)

Where \( \sigma_i c \) and \( \sigma_e c \) are the ionic and electronic conductivities of the coating material respectively. It can be assumed for most effective coating materials that \( \sigma_e c >> \sigma_i c \) and thus the rate constant for the coating can be simplified to:

\[ k_c = \frac{EV_M}{2F} \sigma_i c \]

Thus, the rate constant of the coating is dictated only by the ionic conductivity of the coating. Equation 1 can then be re-written:

\[ x_f = \sqrt{k_f x_e^2 + k_f x_c^2 H - k_f x_c} \]

The equation can then be solved for two limiting cases as follows:

1) When \( k_c x_e^2 << k_c^2 t \):

Equation 4 simplifies to:

\[ x_f = \sqrt{k_f t} \]

As can be seen, all of the coating terms drop out of the equation, thus essentially leaving a scenerio where the coating does not contribute to the oxidation kinetics.
2) When $k_1 x_c^2 >> k_c^2 t$:

In this case it is easier to simplify by plugging back into equation 1, by simplifying we get:

$$x_f = \frac{k_c}{2x_c} t$$

This scenario presents a case where the coating controls the oxidation kinetics of the system and is solely related to the coating kinetic parameter, the coating thickness and the oxidation time [30]. In this $\text{Cr}_2\text{O}_3$ growth kinetics are linear with time, which is inconsistent with much of the data given for coated alloys that show parabolic trends.

This basic model makes many simplified assumptions, and does not take into account the Cr-rich spinel phases that have been experimentally observed to form as a reaction product between the $\text{Cr}_2\text{O}_3$ and MCO spinel coatings.

Previous work on comparisons of different Ni-Cr superalloys speculates that H230 and Hastelloy X have slower oxidation kinetics than Inconel 625 and Inconel 718 due to the formation of $\text{Mn}_{1+\delta}\text{Cr}_{2-\delta}\text{O}_{4+\lambda}$ [52]. In light of this, Chen et. al. developed a 3 layered equivalent circuit model to account for the Cr-rich spinel phase formed during heat-treatment. The model was solved for two cases, one where the Cr-rich spinel layer thickness is small and constant. In this case the oxidation kinetics are found to be dominated by $\text{Cr}_2\text{O}_3$ growth. The second case is where the $\text{Cr}_2\text{O}_3$ scale thickness is small and constant and the Cr-spinel intermediate layer dominates. It was found that in this case the kinetics still follow a parabolic relationship which is a function of the $\text{Cr}^{3+}$ and $\text{O}^{2-}$ conductivities through the coating and Cr-spinel layer [48]. This is likely a more realistic prediction since Crofer 22 and H230 systems coated with MCO have both been shown to have oxidation kinetics that follow a parabolic relationship. This model fits well with experimental observations of MCO coatings on Crofer 22 and H230. Coated Crofer seems
to fit well with Case 2, as the MCO coating resulted in a factor of 5.5 decrease in oxidation kinetics compared to bare Crofer 22 oxidation. Meanwhile, the MCO coated H230 alloy shows very little change in oxidation kinetics, indicating that it may have a thinner Cr-spinel reaction layer [48].

Figure 2.1: A schematic diagram of the transport processes through an SOFC interconnect oxide scale and coating. Reproduced from [24].
Figure 2.2: A schematic diagram of the magnetron sputtering process. Reproduced from [40].

Figure 2.3: A schematic diagram of an MOCVD apparatus. Reproduced from [36].
Figure 2.4: X-section SEM images of MCO coating (a) after reduction heat treatment in 2.75% H₂/Ar at 800 °C for 24 hrs.; (b) the same sample after oxidation in air at 800 °C for 100 hrs.

Reproduced from [24].

Figure 2.5: A schematic diagram of a coated metal foil. X_c and X_f are coating thickness and oxide scale thickness respectively. Reproduced from [30].
Table 2.1: Thermal expansion and conductivity data for some typical SOFC interconnect coatings. Reproduced from [22].

<table>
<thead>
<tr>
<th>Name</th>
<th>$\alpha \times 10^{-6} \ \text{K}^{-1} (\Delta T, ^\circ \text{C})$</th>
<th>$\sigma (\text{S cm}^{-1} \ \text{T} (^\circ \text{C})$</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>SYSZ</td>
<td>10.8 (20–800) [47]</td>
<td>$(3.2–4.5) \times 10^{-7} (800) [48]$</td>
<td>Electrolyte</td>
</tr>
<tr>
<td>Crofer 22 APU</td>
<td>12.0 (20–800) [49]</td>
<td>$8.10 \times 10^{3} (800) [49]$</td>
<td>Interconnect</td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>9.6 (20–1400) [50]</td>
<td>1.28 (250) [50]</td>
<td>Oxide scale</td>
</tr>
<tr>
<td>MnCr$_2$O$_4$</td>
<td>7.2 (25–900) [43]</td>
<td>0.22 (250) [43]</td>
<td>Oxide scale</td>
</tr>
<tr>
<td>Mn$_2$Cr$_2$O$_7$</td>
<td>7.2 (25–900) [43]</td>
<td>12.8–30 (250) [43]</td>
<td>Oxide scale</td>
</tr>
<tr>
<td>Fe</td>
<td>14.0 (20–400) [51]</td>
<td>1.71 (800) [51]</td>
<td>Coating</td>
</tr>
<tr>
<td>Co</td>
<td>15.0 (20–400) [51]</td>
<td>15.0 (800) [51]</td>
<td>Coating</td>
</tr>
<tr>
<td>CoO$_2$</td>
<td>–</td>
<td>35.5 (800) [52]</td>
<td>Coating</td>
</tr>
<tr>
<td>CoCr$_2$O$_4$</td>
<td>7.4 (25–900) [43]</td>
<td>1.92 (750) [43]</td>
<td>Coating</td>
</tr>
<tr>
<td>Ni</td>
<td>16.3 (20–900) [51]</td>
<td>2.20 (1000) [51]</td>
<td>Coating</td>
</tr>
<tr>
<td>NiO</td>
<td>11.5 (100–1000) [50]</td>
<td>14.8 (900) [50]</td>
<td>Coating</td>
</tr>
<tr>
<td>NiCr$_2$O$_4$</td>
<td>7.8 (25–900) [43]</td>
<td>62.5 (250) [43]</td>
<td>Coating</td>
</tr>
<tr>
<td>Cu</td>
<td>20.3 (20–1000) [51]</td>
<td>1.23 $\times 10^{3}$ (977) [51]</td>
<td>Coating</td>
</tr>
<tr>
<td>CuO</td>
<td>–</td>
<td>2 $\times 10^{3}$ (700) [50]</td>
<td>Coating</td>
</tr>
<tr>
<td>LSC-90</td>
<td>9.8–11.2 (20–1000) [53]</td>
<td>10–40 (1000) [53]</td>
<td>Coating/interconnect</td>
</tr>
<tr>
<td>LMAO-DLR</td>
<td>–</td>
<td>–</td>
<td>Coating/interconnect</td>
</tr>
<tr>
<td>LSM-80</td>
<td>11.4 (50–1000) [54]</td>
<td>125 (1000) [55]</td>
<td>Coating/cathode</td>
</tr>
<tr>
<td>LSM-65</td>
<td>12.3 (35–800) [47]</td>
<td>3.70 (800) [56]</td>
<td>Coating/cathode</td>
</tr>
</tbody>
</table>
Chapter 3: Experimental Method

The various experimental methods involved in coating slurry preparation, application, densification and characterization are included in the section that follows. In addition, the procedures used to determine the oxidation kinetics and scale conductivity via area specific resistance (ASR) testing will be described. Finally, a detailed description of the characterization tools utilized in this thesis will be given. The resulting microstructures of coated and un-coated alloys were examined using: optical microscopy, scanning electron microscopy (SEM), focused ion beam (FIB), X-ray diffraction (XRD), transmission electron microscopy (TEM) and energy dispersive x-ray spectroscopy (EDXS).

3.1 Preparation of Mn$_{1.5}$Co$_{1.5}$O$_4$ Slurry

Mn$_{1.5}$Co$_{1.5}$O$_4$ (MCO) slurries were fabricated by mixing commercially available Praxair MCO powder using the following recipe:

1) Mix 57 g of MCO powder with 32 g of V-006 solvent
2) Add 3.2 g of RV-372 (turpineol)
3) Add 32 g of isopropanol
4) Add approximately 50 alumina balls to plastic bottle and ball mill on roller table for 24 hours.

The slurry was kept capped when not in use and was always used within 30 minutes of removal from the ball mill. An additional 24 hr. ball milling procedure always preceded subsequent use of the MCO slurry at a later time.

3.2 Slurry Coating of Crofer 22 APU and Haynes 230 Coupons

Coupons of Crofer 22 APU (0.5 mm thick) and H230 (0.7 mm thick) were cut into 25 mm x 25 mm pieces. The surface of each coupon was ground using SiC grinding paper using
successively finer grit papers (320, 600, 1200), followed by polishing with 6 μm diamond paste. Prior to coating the coupons, any residue from polishing was removed by: ultrasonication in acetone, rinsing in isopropanol and allowing the coupons to dry. Coupons were then dipped into the slurry coating and dried in an oven at 100 °C for 2 hrs. standing up in slotted alumina d-tube.

A reactive sintering process was used in order to densify the MCO coatings, this two-part process consisted of:

1) Reduction of the MCO coating in a sealed tube furnace by heat treating under flowing Ar/3% H₂O/2.75% H₂ at 850 °C for 4 hrs. The initial forming gas mixture was humidified at room temperature by flowing the gas through a water bubbler.

2) Re-oxidation of the MCO coating by heat-treating in air at 850 °C for 4 hrs.

3.3 Heat Treatment Prior to Oxidation of Bare Crofer 22 APU

Square coupons (25 mm x 25 mm) were cut from 0.5 mm thick Crofer22 APU commercial sheet stock. Some of the coupons were heat-treated in a tube furnace under flowing argon for either 1 hour or 4 hours at 1050 °C to modify the initial alloy grain size. This gave three starting conditions for the subsequent oxidation experiments: as-received (AR), heat-treated for 1 hour (HT1h) and heat-treated for 4 hours (HT4h). The surfaces of all of the coupons were then prepared by first mechanically grinding with 600 and 1200 grit SiC, followed by polishing with 6 μm and then 1 μm diamond slurry to obtain a mirror finish.

The oxidation behavior of the samples was evaluated by thermogravimetric analysis. First, the dimensions of each coupon were measured precisely to establish the starting surface area. Triplicate samples for each of the three starting conditions were mounted in a slotted alumina d-tube so that the samples were standing upright. Oxidation tests were performed in a tube furnace
at 800 °C in static laboratory air for up to 750 h. Samples were cooled periodically, removed from the furnace, and weighed using a Delta AT261 Delta Range balance, which has a precision of 0.01 mg.

The effects of pre-oxidation heat-treatment and of thermal exposure during oxidation were evaluated by optical microscopy. Cross-sections through the alloy coupons were prepared using standard metallographic techniques and then etched with oxalic acid to reveal the grain boundaries. Grain diameter measurements were taken from optical microscope images using Image Pro Plus 7 image analysis software. The boundary of each grain was traced in the software and the mean diameter tool was used to obtain the average value of diameters drawn through the grain centroid to the points of intersection on the perimeter in $5^\circ$ increments for each traced grain.

One coupon from each heat-treatment condition was used for microstructural analysis of the oxide scale. X-ray diffractometry (XRD) was performed using an INEL diffractometer with a solid state Curved Position Sensitive Detector (CPSD), which collects data simultaneously over a 2θ range of 20-140°. The oxidized coupons were mounted flat and scanned for a total of 60 minutes using a 30 kV Cu K-α source. The data was analyzed using whole pattern fitting with JADE analysis software. Secondary electron (SE) and backscattered electron (BSE) scanning electron microscopy (SEM) images and Energy Dispersive X-ray Spectrometry (EDXS) analyses of the oxide scales formed were obtained in an FEI Helios 600 Dual Beam focused ion beam (FIB) apparatus equipped with a retractable, low kV, segmented BSE detector and an Oxford 80 mm$^2$ XMax$^N$ Silicon Drift EDXS detector.
Site selective cross-sectional sample preparation for transmission electron microscopy (TEM) was performed using a FEI Strata 400 Dual Beam FIB apparatus equipped with a flip stage for improved final thinning. Firstly, Pt was deposited in situ as a capping layer to protect the original surface of the oxide scale. Rough trench milling was performed at an accelerating voltage of 30 kV with a 2.8 nA ion beam current. Samples were lifted out in-situ using an Omniprobe Autoprobe 200 and attached to a TEM grid using Pt deposited via the ion beam. The Ga⁺ beam currents were successively reduced to 9.5 pA to eliminate milling artifacts in the final specimens. TEM analysis was performed using a Philips CM-200 Supertwin operating at an accelerating voltage of 200 kV and equipped with an EDAX 30 mm² Si(Li) detector for EDXS.

3.4 Reaction Layer Studies on MCO Coated Crofer 22 APU

For this study, square coupons (25 mm x 25 mm) were cut from 0.5 mm thick Crofer22 APU commercial sheet stock. The coupon surfaces were prepared by mechanical grinding with successively finer grades of SiC paper and then polishing with 6 mm diamond paste. This procedure was adopted to eliminate any surface defects due to sheet processing and to ensure that all of the coupons had a consistent surface finish. Prior to applying the coatings, any residue from the polishing process was removed by: ultrasonic cleaning in an acetone bath, rinsing with isopropanol, and allowing the coupons to dry.

Mn1.5Co1.5O4 powder purchased from Praxair was used to form a slurry, which was applied to the polished surfaces of the alloy coupons; this was then converted to densified MCO coatings of approximately 5 mm in final thickness using a variant of the process sequence described by Yang et al. [6]. This sequence comprised: drying in an oven at 100 °C for 2 h;
reducing in a sealed tube furnace under flowing Ar/3%H2O/2.75%H2 at 850 °C for 4 h; and then re-oxidizing in air at 850 °C for 4 h. Subsequent oxidation experiments were performed on the MCO-coated coupons in a tube furnace under flowing air (1.5 L min⁻¹) at 800 °C for times of up to 1000 h. The oxidation kinetics data for the samples considered here were presented in our previous paper [21].

Microstructural analysis was performed on three of the coupons: one was in the as-coated condition (i.e. after the reduction/oxidation reactive sintering treatment but with no subsequent extended exposure), and the other two had been oxidized for a duration of 250 or 1000 h. Cross-sections through the three coupons were mounted in epoxy, ground mechanically using SiC papers, polished to a 0.25 mm finish using diamond pastes, and then carbon coated. Site-selective TEM sample preparation was performed using a FEI Strata 400 Dual Beam FIB equipped with a flip-stage and an STEM detector for improved final thinning. In-situ platinum deposition was performed in order to protect the surface of the TEM specimen during ion milling. Ga⁺ beam currents were reduced iteratively to a value of 9.7 pA during final milling to avoid excessive Ga⁺ implantation and beam damage. TEM foils were mounted onto copper Omni grids at 2 corners in order to limit mechanical buckling of the samples during final thinning.

The samples were examined in a Philips CM-200 supertwin equipped with an EDAX 30 mm² SiLi EDXS detector and operating at an accelerating voltage of 200 kV. Diffraction contrast images and selected area diffraction patterns (SADPs) were obtained in TEM mode while annular dark field (ADF) images and EDXS data were obtained in STEM mode.
3.5 Reaction Layer Studies on MCO Coated H230

Haynes 230 sheet (0.7 mm thick) was purchased from Haynes International and cut into 25 mm x 25 mm coupons. The sample surfaces were ground using 600 and 1200 grit SiC and then polished using 6 μm and 1 μm diamond paste. To remove any residual polishing media, the polished samples were sonicated in acetone, rinsed with isopropanol and allowed to dry.

The oxidation behavior of the uncoated alloy was evaluated by thermogravimetric analysis. First, the dimensions of each coupon were measured precisely to establish the starting surface area. The samples were mounted in a slotted alumina d-tube so that they were standing upright, and oxidation tests were performed in a tube furnace at 800 °C in static laboratory air for up to 1000 h. Samples were cooled periodically, removed from the furnace, and weighed using a Delta AT261 Delta Range balance, which has a precision of 0.01 mg.

Some of the polished coupons were dip-coated with an MCO slurry (Mn$_{1.5}$Co$_{1.5}$O$_4$ from Praxair), and the coating was then densified following the procedure described by Yang et al. [80]. This reactive sintering process involves: drying in an oven at 100°C for 2 h; reducing in a sealed tube furnace under flowing Ar/3%H$_2$O/2.75%H$_2$ at 850 °C for 4 h; and then re-oxidizing in air at 850 °C for 4 h. Metallographic cross-sections were prepared from samples at each stage in the coating process by mounting the coupons in a two-part cold mount epoxy, grinding using successively finer grades of SiC paper, and then polishing using diamond paste down to 0.25 μm. Some of the MCO-coated coupons were also oxidized at 800° C for up to 1000 h in static laboratory air; the thermogravimetric data from these samples were reported in our previous paper [48].
Detailed microstructural analysis was performed on 4 samples: 1) bare H230 oxidized for 1000 h; 2) coated H230 after the reduction process; 3) coated H230 after reduction and re-oxidation processes; and 4) MCO-coated H230 after 1000 h oxidation at 800 °C. Scanning electron microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDXS) were performed using an FEI Helios 600 Dual Beam FIB equipped with: an Oxford X-MaxN 80 mm² silicon drift detector; a solid-state, low-kV, concentric backscattered detector; and a retractable Scanning Transmission Electron Microscopy (STEM) detector. TEM samples were cut from representative regions at the H230/coating interfaces using the following procedure: a 2-3 μm layer of Pt was deposited as a capping layer to protect the original surface of the sample; rough trenches were milled using a 30 kV Ga⁺ beam at a beam current of 2.8 nA; final thinning was performed using a pre-tilted STEM holder by reducing the Ga⁺ beam current to 9.7 pA and finally reducing the accelerating voltage to 5 kV to limit ion beam damage of the samples. Samples were lifted out in-situ using an Omniprobe 200 micromanipulator and welded to two corners to of a copper Omni grid to avoid sample buckling during final thinning.
Chapter 4: Crofer Oxidation and Alloy Microstructural Effects

4.1 Introduction/Preamble

Crofer 22 APU (ThyssenKrupp AG, Germany) is a ferritic stainless steel developed specifically for SOFC interconnect applications [58]. The composition limits for the alloy are given in Table 4.1; the Mn is intended to promote the formation of a (Mn,Cr)\(_3\)O\(_4\) spinel overlayer on top of the chromia scale and thus to obviate the need for a protective coating. Yang et al. measured an oxidation rate constant (\(k_g\)) of 8.0x10\(^{-14}\) g cm\(^{-4}\) s\(^{-1}\) for Crofer 22 APU oxidized in air at 800 °C [34], and this falls within the range of rate constants reported for ferritic stainless steels in a review by Fergus [9]. Unfortunately, this oxidation rate is not sufficiently low to enable uncoated Crofer 22 APU interconnects to meet the current 40,000 hour SOFC lifetime requirement. Life prediction models based on thermal expansion and residual stress calculations performed by Liu et al. indicated that the maximum allowable oxide scale thickness to avoid oxide spallation is around 11 µm [29]. Using the oxidation rate constant measured by Yang et al., this would imply that scale formed on Crofer 22 APU would become mechanically unstable after less than 5000 h exposure. Moreover, SOFC tests performed by Stanislowski et al. using bare Crofer showed a performance degradation rate of 21%/1000 h [22]; this rate is two orders of magnitude higher than the value that can be tolerated for long-term SOFC applications. Thus, as for all other SOFC interconnect alloys, Crofer 22 APU requires a protective coating both to retard the oxidation rate and to prevent the egress of volatile chromium species. The requirements for such coatings are rather stringent. They must be: electrically conductive, oxidation resistant, and have minimal open porosity. The most successful coatings to date have been based on manganese cobaltite ((Mn,Co)\(_3\)O\(_4\) - MCO). The MCO composition that has
received most attention is Mn$_{1.5}$Co$_{1.5}$O$_4$, which exhibits electrical conductivities of $> 60$ S/cm at 800 °C [25].

In recent work by the present authors [59] Mn$_{1.5}$Co$_{1.5}$O$_4$ coatings were applied to Crofer 22 APU samples using the slurry coating process described by Yang et al. [25]. The coated samples were oxidized at 800°C in air for times of up to 1000 h and the microstructures of the as-deposited and the oxidized coatings were analyzed by cross-sectional transmission electron microscopy (TEM). It was shown that a complex series of spinel reaction products developed between the MCO coating and the Crofer substrate; these included (Mn,Co,Cr,Fe)$_3$O$_4$ layers between the chromia and the MCO and pockets of stoichiometric MnCr$_2$O$_4$ at the chromia/alloy interface. These reaction products could have important consequences for the degradation of MCO-coated Crofer interconnects during long-term service in SOFCs, but a full elucidation of these phenomena will require a more detailed understanding of the basic oxidation characteristics for Crofer 22 APU than is currently available in the literature.

In previous oxidation studies it has been shown that a two-layer scale forms on Crofer 22 APU. This microstructure comprises a compact Cr$_2$O$_3$ layer on the metallic substrate and an outer (MnCr)$_3$O$_4$ spinel phase on top of the Cr$_2$O$_3$, as intended by the alloy designers. An XRD study of scale development on Crofer 22 APU at 800 °C by Yang et. al. showed that both Cr$_2$O$_3$ and (Mn,Cr)$_3$O$_4$ formed after only 2 hours of exposure in air [50]. The same two oxidation products have also been reported as being stable in dual atmosphere (moist H$_2$/air) [61] and in SO$_2$ containing atmospheres [62]. While there have been several published oxidation studies on Crofer 22 APU, to our knowledge there have been no investigations on the effects of alloy microstructure on oxidation kinetics and scale morphology.
In this paper, we describe a study of the microstructure in the oxide scale formed on Crofer 22 APU in static air at 800°C. Crofer samples were used in both the as-received (cold-worked and recovered) condition and after pre-oxidation heat treatment to modify the grain size. It is well known that alloy grain boundaries can act as rapid diffusion paths for both anions and cations, and so the starting alloy grain size could have a profound influence on the nucleation and growth of the native oxide scale. However, it is not clear what this effect will be: some literature suggests that a smaller alloy grain size leads to improved oxidation resistance [63], whereas others have shown just the opposite [64]. Here we show that a larger grain size leads to a dramatic reduction in the oxidation rate for Crofer 22 APU and that this is accompanied by changes in the character and morphology of the oxide scale. These observations are used to deduce the role that grain boundary diffusion plays in oxide scale development and to provide a useful baseline for comparison with the microstructures in the oxide scales of coated Crofer 22 APU samples.

4.2 Results

4.2.1 Pre-Heat Treatment Effect on Alloy Microstructure

The grain structures corresponding to the three heat-treatment conditions (AR, HT1h, HT4h) were evaluated before and after oxidation by optical microscopy on metallographic cross-sections. Representative images are shown in Figure 4.1: Figures 4.1(a), (c) and (e) are examples of the grain structures exhibited before oxidation by the AR, HT1h and HT4h coupons, respectively; Figures 4.1 (b), (d) and (f) are the corresponding structures for the coupons oxidized at 800°C for 750 h. Values of the grain diameter were obtained from these samples by
taking the mean of the mean diameter value for 30-250 individual grains depending upon the sizes of the grains. The grain diameters for the three samples before oxidation were 15.9, 73.7 and 248.6 µm for the AR, HT1h and HT4h coupons, respectively. Thus, the pre-oxidation heat-treatment had the intended effect of growing the grains significantly to produce three rather different starting grain sizes. There was also significant grain growth during the oxidation for the AR and HT1h samples, but not the HT4h sample. The grain diameter for the AR sample after oxidation at 800°C for 750 h was 90.2 µm; this corresponds to a six fold increase in grain diameter over the unexposed AR sample. For the HT1h samples, both the initial and final grain diameters were larger than those for the AR samples, but the final grain diameter of 192.7 µm was less than three times the initial value. For the HT4h condition the final grain diameter was 244.1 µm, which is very similar to the initial value for this material.

4.2.2 Oxidation Kinetics

From the thermogravimetric data it was found that, in each case, parabolic oxidation behavior was established after an initial transient. This is revealed most clearly in plots of weight gain squared against time, as shown in Figure 4.2. Each of the sets of samples show a variation in the rate of weight gain up to 250 h, after which weight gain squared varies linearly with time. This is what one would expect from Wagner’s theory of parabolic oxidation

\[(w/A)^2 = k_g t\]

where \(w\) is the weight gain, \(A\) is the specimen surface area, \(k_g\) is the parabolic rate constant, and \(t\) is the oxidation time. Using the linear portions of the plots from 250 h to 750 h we obtained values of \(k_g = 4.82 \times 10^{-8}, 2.82 \times 10^{-8} \text{ and } 1.41 \times 10^{-8} \text{ mg}^2\text{cm}^{-4}\text{s}^{-1}\) for the AR, HT1h and HT4h
samples, respectively. We note that this reduction in $k_g$ is very significant and indeed this is comparable to the values obtained by applying MCO coatings to Crofer22 APU in our previous studies ($k_g = 1.45 \times 10^{-8} \text{ mg}^2\text{cm}^4\text{s}^{-1}$ at 800°C [48]). The microstructural data presented below were acquired to reveal the origins of this improvement in oxidation resistance.

### 4.2.3 Plan View Characterization of Oxide Scales (XRD and SEM)

The X-ray diffraction data obtained from the oxidized AR, HT1h and HT4h coupons are shown in Figure 4.3. Peak fitting using the ICDD database indicated that the major phases present in each case are rhombohedral Cr$_2$O$_3$, cubic MnCr$_2$O$_4$ spinel and body-centered-cubic α-Fe. The relative intensities of the peaks were used to estimate the volume fractions of the phases, and the values obtained were: 62.8% MnCr$_2$O$_4$, 32.4% Cr$_2$O$_3$ and 4.8 % α-Fe for the AR sample; 64.7% MnCr$_2$O$_4$, 30.0% Cr$_2$O$_3$ and 5.3 % α-Fe for the HT1h sample; and 78.8% MnCr$_2$O$_4$, 14.0% Cr$_2$O$_3$ and 7.2 % α-Fe for the HT4h sample.

The distribution of these phases was inferred from SEM analysis on the surfaces of the oxide scales. Representative BSE SEM images obtained from the AR, HT1h and HT4h coupons oxidized at 800°C for 750 h are shown in Figure 4.4. In each case the scale is comprised of larger octahedral crystals with smaller particles having a less well-defined morphology between these octahedra. Qualitative EDXS data indicate that the large octahedra are the MnCr$_2$O$_4$ phase, the finer particles are the Cr$_2$O$_3$, and that there are no isolated regions of exposed α-Fe. Thus, the presence of α-Fe peaks in the XRD data must correspond to contributions from the underlying Crofer substrate. The main differences between the oxide scales for the three samples are the dimensions and coverage of the MnCr$_2$O$_4$ octahedra; the sizes of these features were 0.3-1.5 μm for the AR sample, 0.8-2.1 μm for the HT1h sample and 0.9-3.8 μm for the HT4h sample. It is
difficult to estimate the MnCr$_2$O$_4$ coverage accurately from such images but it is clear that this phase constitutes a larger proportion of the exposed surface area of the scale for the HT4h sample than for the AR or HT1h samples.

4.2.4 TEM Microstructural and Chemical Analysis of Oxide Scales

The details of the scale microstructures were revealed using TEM and STEM analyses of FIB-cut cross-sections through the scales. Examples of the TEM and STEM data obtained from the AR sample oxidized at 800 °C for 750 h are shown in Figures 4.5 and 4.6, respectively. Figure 5(a) is a bright field TEM image of the scale morphology and Figures 4.5(b)-(d) are representative selected area diffraction patterns (SADPs) obtained from the three distinct microstructural regions in the scale labeled 1, 2 and 3, respectively in Figure 4.5(a). Region 1 is a coarse grained outer layer and the SADPs obtained from these grains correspond to those expected for a cubic spinel phase having a lattice parameter of $a_0 = 0.836$ nm. The EDXS data obtained from such grains are consistent with this phase being MnCr$_2$O$_4$ with a small amount (1-3 wt.%) of Fe. Region 2 is a fine-grained layer below the MnCr$_2$O$_4$. The grains are too small for the acquisition of single-crystal zone axis SADPs, but all of the diffraction spots in patterns such as Figure 4.5(c) lie on rings corresponding to strongly diffracting planes in Cr$_2$O$_3$ with the corundum structure ($a_0 = 0.496$ nm, $c_0 = 1.359$ nm). The EDXS measurements obtained from this layer indicated that this chromia layer contained approximately 1 wt.% Ti. Region 3 is an example of a sub-scale oxide pocket that protrudes into the substrate from the chromia/alloy interface. The SADPs and EDXS data obtained from such pockets indicated that, like region 1, these were cubic MnCr$_2$O$_4$ spinel with a small amount of Fe incorporated into the lattice, although in these cases the Fe content was less than 1 wt.%.
The distribution of the phases in the scale for the AR sample was rather inhomogeneous. To show this more clearly, STEM X-ray maps were acquired from the FIB-cut sections. Figure 4.6 is an example of these data obtained from approximately the same region as Fig 5; this comprises a BF STEM image of the region analyzed together with maps for Cr, Mn, Fe, O and Ti. Each map corresponds to a grid of 256 x 200 measurements of the counts within a 100 eV window centered on the Kα1 energy for that element. The data were acquired by scanning the region 2048 times with a dwell time of 0.2 ms per measurement for a total acquisition time of around 5.8 h corresponding to just over 0.4 s per pixel. From the Cr and O maps, it is clear that the thickness of the Cr2O3 scale varies from approximately 250 nm on the right-hand side of the mapped region to over 3 μm on the left. Such observations revealed that the Cr2O3 scale was thinner in the regions where external MnCr2O4 spinel was present. The regions between the MnCr2O4 exhibited a much thicker Cr2O3 scale with embedded Fe-rich pockets. The composition of these pockets measured by EDXS was consistent with the bulk composition of Crofer 22 APU. The Ti and O maps show a very finely dispersed internal oxide phase forming below the Cr2O3 scale within the Fe-Cr matrix. The Mn and Cr maps clearly reveal the presence of MnCr2O4 subscale spinel pockets 500-1000 nm in diameter between the Cr2O3 scale and the Crofer substrate. We note that while the chemistry and crystal structure of the inner and outer MnCr2O4 are rather similar, there is a clear difference in morphology: the sub-scale spinel pockets are more equi-axed, whereas the outer spinel layer exhibits pronounced crystallographic facets.

Representative bright field TEM images obtained from FIB-cut cross sections through the oxidized HT1h and HT4h samples are shown in Figure 4.7. In both cases, the same three microstructural regions (outer MnCr2O4, Cr2O3 layer and sub-scale MnCr2O4 pockets) were
observed in the oxide scale, but the layers/regions were thinner and distributed more homogeneously than for the AR sample. As such, quantitative EDXS line-scans were acquired (rather than more qualitative X-ray maps such as Figure 4.6) and examples from the oxidized HT1h and HT4h samples are shown in Figures 4.8 and 4.9, respectively.

Figure 4.8(a) is an annular dark field (ADF) STEM image obtained from the FIB-cut cross-section of the oxidized HT1h sample with the alloy on the left-hand side of the image and the oxide scale on the right. Figure 4.8(b) is a compositional profile determined from EDXS measurements obtained along the bright horizontal line indicated in Figure 4.8(a). Spectra were acquired at 10 nm intervals along the line using a 10 nm diameter electron probe with an acquisition time of 3s per spectrum. The integrated intensities in the K peaks for each of the elements were used to perform a standard-less quantification of the data based upon the thin film approximation. The first 500 nm of the linescan plot in Figure 4.8 corresponds to the Crofer with a measured chemistry of 78 wt.% Fe and 22 wt.% Cr. The chromia scale in this location is around 375 nm thick and this contains a small amount (≈ 0.5 wt.%) of Ti. It should be noted that while the chromia scale in this particular area is quite thin, other regions such as those shown in Figure 4.7(a) are much thicker; Cr$_2$O$_3$ layer thicknesses of 300-1200 nm were measured for the HT1h sample. The chemistry for the last 1.5 μm of the linescan shown in Figure 4.8 is consistent with the MnCr$_2$O$_4$ spinel phase. We note that the Fe content in the spinel increases from approximately 1.5 wt.% at the chromia/spinel interface to 4.5 wt.% towards the surface of the spinel.

The corresponding data obtained from the oxidized HT4h sample is shown in Figure 4.9. The first 1 μm of the linescan corresponds to the alloy composition. The next 100 nm is
representative of a subscale MnCr$_2$O$_4$ pocket similar to those observed on the AR sample. The chromia scale in this particular region is approximately 650 nm thick and again contains approximately 0.5 wt.% Ti. Here again, there was significant variation in the thickness of the chromia layer. Indeed, the area shown was the thickest region observed, and in most places the chromia scale was 100-550 nm thick. The final 1.2 μm of the linescan are again consistent with MnCr$_2$O$_4$ spinel, however the Fe content ranges from about 1.0 wt.% near the chromia/spinel interface up to 2.5 wt.% near the surface of the spinel.

4.2.4 Characterization of Internal Oxidation

As shown in Figure 4.6, there are Ti-rich internal oxides within the Crofer 22 APU substrate below the MnCr$_2$O$_4$ / Cr$_2$O$_3$ scale. These internal oxides are extremely fine (≈ 50 nm) in the case of the AR sample, but are up to 300 nm in diameter in the oxidized HT4h sample. While accurate quantitative analysis was challenging for such embedded particles due to interference from the surrounding metallic matrix and to an overlap of the O-K and Ti-L peaks, an average of EDXS measurements taken from the three largest internal oxides gave an O:Ti ratio of 2.28. Since the highest oxidation state for titanium is +4, the obvious conclusion is that these internal oxides are TiO$_2$, but this was not borne out by the electron diffraction data. 4.10 is a BF image from a region in the oxidized HT4h sample that contains two such internal oxide particles, and the inset is a zone axis SADP from one of these particles. All of the particles appeared to be single crystal, but the lattice spacings obtained from the SADPs were not consistent with any of the three known polymorphs of TiO$_2$ (anatase, brookite or rutile). Indeed the only known Ti-O phase that appeared to match the measured lattice spacings is the low-temperature monoclinic polymorph of TiO identified by Watanabe et al. [65] (space group $A2/m$, $a_0$=0.585 nm, $b_0$=0.934 nm, $c_0$=0.414 nm).
4.2.5 Short-Term Oxidation Studies

Although the observations on samples oxidized for 750 h revealed significant differences between the oxide scales for the three alloy conditions, there was no obvious mechanistic link between these features and the measured change in parabolic rate constant. To investigate this phenomenon further, additional samples were prepared and oxidized under the same conditions, but the samples were withdrawn for microstructural analysis after just 5 h.

Figure 4.11(a) is a low voltage (2 kV) SE SEM image of the scale formed on the AR sample after 5 h of oxidation. At this stage, there are already large (300-650 nm) faceted spinel particles that partially cover a fine-grained chromia scale, and the arrangement of these particles suggests strongly that they have formed preferentially at locations where the alloy grain boundaries intersect the surface. To verify this, SE SEM images were obtained from the polished face of FIB-milled trenches cut into the sample surface. One such image is shown in Figure 4.11(b). The chromia scale is just 30-50 nm thick in such regions and it is clear that a large spinel particle lies at the point where a grain boundary in the alloy intersects the surface. The chemistry of the oxide scale is revealed most clearly in X-ray maps obtained from the sample surfaces, and one example is shown in Figure 4.12. This comprises an SE SEM image and maps for Cr, Fe, Mn, O and Ti. Each map corresponds to a grid of 512 x 400 spectra acquired over an area of 26.6 x 20.8 μm. Due to the extremely high count rate for the SDD EDXS detector (150,000 counts/s) full spectral information could be acquired in a single scan with a dwell time of 3 ms per pixel, corresponding to a total acquisition time of 10 min. Unlike the STEM maps shown in Figure 4.6, the map intensities shown here are proportional to the corresponding compositions obtained from quantitative analysis of the spectra. The maps show
strong enhancement of Cr, Mn and O at the boundaries consistent with the preferential formation of MnCr$_2$O$_4$ at these locations. The Fe map shows a complementary trend; this is consistent with the Fe signal arising from the underlying alloy being strongly excited through the thinner chromia scale but less so through the thicker spinel at the emergent alloy grain boundaries.

Corresponding data from the HT4h sample after 5 h of oxidation are shown in Figures 4.13 and 4.14. The polyhedral spinel particles are present on the surface of the scale as shown in Figure 4.13(a), but the particles are smaller (175-500 nm) and cover less of the alloy surface area than for the AR sample (Figure 4.11(a)). SE SEM images such as Figure 4.13(b) obtained from FIB-cut cross-sections show a much thicker chromia scale (90-275 nm). Since the alloy grain size is far larger than the field of view in such images, no grain boundaries were observed in such sections, however examples of the faceted spinel particles were still present in such region. The distribution of the spinel particles was revealed clearly in SE SEM images and X-ray maps obtained from the sample surfaces (e.g. Figure 4.14). These spinel particles are dispersed much more homogeneously across the alloy surface than for the AR sample shown in Figure 4.12.

4.3 Discussion

It is clear from the data presented in the previous section that the pre-heat treatment of Crofer 22 APU has a profound effect on the oxidation kinetics and on the microstructural development of the oxide scale. In the sections that follow we discuss the possible mechanisms involved in the development of these microstructures and their implications for long-term SOFC durability. Firstly, we consider the way in which the microstructure develops on the AR samples. The effects of pre-oxidation heat treatment are then discussed. These observations are
compared to our previous studies on MCO-coated Crofer 22 APU, and finally the implications of these observations for SOFC performance are noted.

4.3.1 Microstructure and Scale Development of AR Crofer 22 APU

The main microstructural features observed in the oxide scales that develop on the AR samples are a continuous Cr$_2$O$_3$ layer in contact with the alloy substrate and a discontinuous MnCr$_2$O$_4$ layer on top of the Cr$_2$O$_3$. There are also two types of internal oxides: MnCr$_2$O$_4$ pockets which form between the alloy substrate and the Cr$_2$O$_3$ scale, and small (≈50 nm) equi-axed Ti-rich oxide precipitates. In addition to these various types of oxides there are metallic inclusions within the Cr$_2$O$_3$ scale for the AR samples.

There are numerous examples in the literature of ferritic stainless steels that form two-layer oxide scales, and the alloy that has received the most attention is SS 430 [66-68]. Such Fe-Cr-Mn alloys form an initial Cr$_2$O$_3$ layer very rapidly during oxidation. Saeki used a combination of X-ray photoelectron spectrometry and XRD to characterize the oxides formed on SS 430 in O$_2$/N$_2$ at 1000 °C for up 20 min [67]. It was found that during the first 15-30 s of oxidation, only a single-phase oxide layer with the corundum structure is present. Initially this layer has a chemical composition close to Fe$_2$O$_3$, but this changes rapidly to Cr$_2$O$_3$. After 30 s of oxidation an MnCr$_2$O$_4$ spinel phase was observed which also corresponded to a change in the oxidation state of Mn from +3 (Mn$_2$O$_3$) to +2 (MnCr$_2$O$_4$). It was proposed that the induction period for the formation of the spinel corresponded to the time taken for Mn$_2$O$_3$ to reach its maximum solubility in Cr$_2$O$_3$ (12-17 wt.%). Once this value was exceeded, the MnCr$_2$O$_4$ spinel nucleated on the surface and grew via a reaction between Mn$_2$O$_3$ and Cr$_2$O$_3$ [66,67]. If this is the mechanism by which the two-phase scale forms on the Crofer 22APU samples considered in this study then the scale microstructure may be dictated by the initial nucleation rate for the chromia.
This is because the nucleation rate will determine the chromia grain size, and grain boundary diffusion of transition metals through Cr$_2$O$_3$ is 3-5 orders of magnitude faster than bulk diffusion [69]. Moreover, it has been reported that grain boundary diffusion of Mn is 1-2 orders of magnitude faster than grain boundary diffusion of Cr or Fe in Cr$_2$O$_3$ [69,70].

Our observations of the scale formed after just 5 h oxidation of the AR sample (Figures 4.11 and 4.12) indicate that outward Mn and Cr diffusion via chromia grain boundaries is initially extremely rapid, resulting in the formation of a substantial amount of MnCr$_2$O$_4$ phase. The subsequent growth of the outer spinel layer must be dramatically slower because there are still some unoccluded regions of chromia on the surface after 750 h (Figure 4.3). It is interesting to note that in a previous study on high temperature oxidation of Fe-Cr-Mn systems by Cox et al. [71] a change in the parabolic rate constant after a particular exposure time was attributed to the point at which there is complete surface coverage by the Mn-Cr spinel. At this stage the oxidation rate would no longer be solely controlled by outward diffusion of Cr$^{3+}$ through the Cr$_2$O$_3$ as it is initially. Although a similar change in parabolic rate constant was observed at 250 h for the AR samples in the current work, this is clearly not due to spinel coverage alone because complete surface coverage by spinel has not been achieved at this point. Since there is only $\approx$ 0.5 wt.% Mn in the alloy, it seems more likely that the change in rate constant at 250 h occurs due to a depletion of the Mn in the alloy. Indeed, a similar change in parabolic rate constant has been observed by Kim et al. [72] on Haynes 230, which is another alloy which forms a two-layer Cr$_2$O$_3$/MnCr$_2$O$_4$ scale. This change in kinetics was attributed to complete oxidation and depletion of the initial Mn source in the alloy. Since the MnCr$_2$O$_4$ spinel forms preferentially at the emergent alloy grain boundaries, it is clear that Mn diffuses more rapidly along these boundaries than through the grains as one might expect. Thus the alloy grain size would dictate
the total oxidation time required to deplete the Mn. Beyond this point, the measured oxidation kinetics are presumably dominated by the transport of chromium through the alloy and the scale.

The subscale MnCr$_2$O$_4$ pockets observed in this study are similar to those found in our previous study on MCO-coated Crofer 22 APU [59] and in numerous other studies on similar alloy systems [37, 71, 73]. Cox et. al. proposed that this subscale spinel phase may be formed during the early stages of oxidation due to vacancy coalescence and void formation below the chromia scale. Such voids could cause the thin chromia scale to crack, exposing the underlying alloy to the oxidizing atmosphere. The local increase in O$_2$ partial pressure in a region depleted in Cr may favor the formation of MnCr$_2$O$_4$ [71]. This mechanism would lead to the majority of these subscale pockets being formed during the earliest stages of oxidation when the chromia scale is still quite thin. We note that in the current study the subscale spinel pockets were observed even after 5 h exposure, and that they showed a propensity to form near alloy grain boundaries.

The formation of Ti-rich internal oxides in the AR samples during oxidation is consistent with a previous report by Froitzheim et al. [8] on oxidation microstructures for related Fe-Cr-Mn alloys oxidized at 1000°C in laboratory air. In this previous study, it was concluded that the internal oxides were probably Ti$_2$O$_3$ and/or Ti$_3$O$_5$. In the present case, the electron diffraction data are not consistent with either of these phases or indeed any of the known polymorphs for TiO$_2$, despite this being the stoichiometry suggested by the EDXS data. The SADPs instead correspond to the monoclinic polymorph of TiO first identified by Watanabe et al. [65]. This structure is a defect analog of the NaCl-type structure and can be produced from the parent structure by ordering of approximately 15% vacancies on the lattice sites of the cubic parent structure (e.g. [74]). Due to the defect character of the structure, it can accommodate significant
deviations from stoichiometry giving compositions TiO$_x$ with $x = 0.7 – 1.25$. We note that while the measured compositions for the internal oxides fall well outside this range, there is considerable uncertainty in the measurements due to the size of the particles and to an overlap of the O-K and Ti-L peaks.

The metallic inclusions/protrusions observed in the chromia scale (e.g. Figure 4.6) are similar to those reported elsewhere in the literature for various alloy systems [37,62, 73, 75, 76]. All of these previous works attribute the metallic inclusions to stresses that arise from internal oxidation of titanium or the formation of MnCr$_2$O$_4$ subscale pockets. Issartel et al. accounted for these stresses on the basis of the Pilling-Bedworth ratio for these internal oxidation reactions [76]. They showed that a combination of compressive stresses in the oxide, tensile stresses in the alloy, and small pre-existing undulations on the alloy surface could lead to extrusion of the metal into the scale adjacent to internal oxides in SS 439 and SS 441 [76]. Our observations of metallic protrusions forming directly between MnCr$_2$O$_4$ subscale spinel pockets, such as in Figure 4.6, are consistent with this mechanism. While these metallic protrusions may provide “keying” or interlocking with the oxide scale during short-term exposure studies, they could potentially be detrimental during long-term exposure, as they would act as stress-risers and potential sites for localized scale spallation.

4.3.2 Effect of Pre-Oxidation on Oxidation Kinetics and Microstructure

The most obvious effect of the pre-oxidation heat treatment of the Crofer 22 APU at 1050 °C in argon is the growth of the initial alloy grain size from an average of 15.9 μm in the AR sample to 73.7 μm and 248.6 μm in the HT1h and HT4h samples respectively. While the AR and HT4h samples exhibit fairly consistent grain sizes through the coupon thickness, the HT1h sample clearly has finer grains at the surface than within the center of the coupon. There are two
main ways in which such an anisotropic grain size distribution could arise. Firstly, grain boundary / surface interactions could inhibit the growth of near-surface grains, leading to a smaller grain size at the surface during the initial stages of grain growth. Secondly, if the dislocation densities at the surface are higher than within the bulk of coupons then the near-surface grains could undergo recrystallization prior to grain growth while recovery and grain growth processes operate throughout the remainder of the material. Although the latter processes would seem to be the best explanation for the observed grain structure, we note that the AR sheet stock is provided in the recovered/annealed condition and so the residual defect density should be too low for recrystallization to occur.

The main features of the oxide scale microstructures on the HT1h and HT4h samples are the same as for the AR samples. Thus, there is a continuous Cr$_2$O$_3$ layer on the alloy with an outer discontinuous MnCr$_2$O$_4$ spinel layer, subscale pockets of MnCr$_2$O$_4$, and Ti-rich internal oxide precipitates in the alloy below the scale. It should be noted that the Ti-rich internal oxides are present in the unoxidized HT1h and HT4h samples, as seen in Figure 4.1. Since these internal oxides must form due to oxygen pick-up during heat-treatment, the contribution of such oxides to the total weight gain would not be incorporated into the thermo-gravimetric measurements. While this effect might lead to an underestimate of the total weight gain, even if all of the Ti were consumed in the formation of such internal oxides then this would only account for a small proportion of the difference in $k_g$ between the AR and HT4h samples. The presence of around 0.5% Ti in the chromia demonstrates that there must be a lower volume fraction of TiO$_x$ than this analysis would imply and so we can neglect this effect as a major cause of the differences in the measured values of $k_g$. 

64
The most significant difference between the scale microstructures for the AR and the HT1h and HT4h samples is in the size and coverage of the outer spinel layer. The outer MnCr₂O₄ grains were 0.3-1.5 μm for the AR sample, 0.8-2.1 μm for the HT1h sample, and 0.9-3.8 μm for the HT4h sample (Figure 4.3). Coverage was difficult to measure accurately, but the XRD analysis showed an increase in the proportion of the volume sampled that corresponded to MnCr₂O₄ from 62.8% in the AR sample to 64.7% for HT1h and 78.8% for HT4h. The way in which these differences arise can be inferred from the microstructures of the scales formed on the AR and HT4h samples after just 5 h oxidation at 800 °C. It is clear that the chromia scale on the AR sample is much thinner than that on the HT4h sample after 5 h. This would indicate that the Cr₂O₃ nucleation rate was higher on the AR sample, leading to a finer-grained chromia scale during initial oxidation. In addition, the finer alloy grains in the AR sample would allow for more rapid transport of Mn to the surface of the alloy where it would react to form MnCr₂O₄, thereby depleting the reservoir of Cr available to form Cr₂O₃. Initially this thinner chromia scale leads to the formation of larger and more numerous MnCr₂O₄ nuclei on the AR sample. After 750 h oxidation, however, the smaller nuclei on the HT4h sample had grown into larger spinel grains covering more of the sample surface. Since the long-term oxidation kinetics are dominated by grain boundary diffusion through the Cr₂O₃ and MnCr₂O₄, the larger outer spinel grains formed on the HT4h sample would provide fewer preferential diffusional paths for oxygen ingress. This is presumably the reason why the HT4h samples exhibited a 3.5x lower value of $k_g$ than the AR samples.

4.3.3 Comparison of Bare and MCO Coated Crofer 22 APU

In previous studies by the current authors it was found that oxidation of MCO-coated Crofer 22 APU in air led to the formation of scales with many similar features to those observed
in this study [48,59]. Thus, the coated samples formed: continuous chromia scales at the alloy/coating interface, sub-scale MnCr$_2$O$_4$ pockets and equi-axed internal TiO$_x$ precipitates. Since these phases also form in the absence of an MCO coating, they are clearly inherent to the oxidation of Crofer 22 APU. In the MCO-coated alloy, however, a thick (≈ 5 μm) reaction layer (RL) formed between the Crofer 22 APU and the MCO after 1000 h oxidation at 800 °C, resulting in a 5.5x reduction in $k_g$ compared to bare (as-received) Crofer 22 APU [48]. The details of the complex RL formed on MCO coated Crofer 22 APU were recently studied in greater detail [59], and it was observed that after 1000 h oxidation at 800 °C the RL comprised a cubic spinel with a chemistry of Mn$_{1.38}$Co$_{0.84}$Cr$_{0.54}$Fe$_{0.24}$O$_4$ [59]. While it is thermodynamically favorable to form an MnCr$_2$O$_4$ outer spinel on bare Crofer 22 APU, the presence of the (Mn,Co,Cr,Fe)$_3$O$_4$ RL in direct contact with Cr$_2$O$_3$ indicates that this mixed RL spinel is more thermodynamically stable than MnCr$_2$O$_4$ in the MCO-coated Crofer system. It has been previously proposed by Fergus et al. that the RL grows by concurrent inward migration of the RL/Cr$_2$O$_3$ and Cr$_2$O$_3$/alloy interfaces [77,78]. Additional work is necessary to determine how alloy pre-heat treatment may impact the thickness and chemistry of the RLs formed between Crofer 22 APU and MCO, however it is tempting to speculate that the alloys subjected to a pre-oxidation heat treatment, which resulted in a greater volume of MnCr$_2$O$_4$ outer spinel, may indeed produce thicker RLs.

**4.3.4 Implications for SOFC Performance**

The benefits of utilizing an alloy that forms an MnCr$_2$O$_4$ outer spinel scale have been shown previously in a study by Yang et al. [50] in which a decrease in area specific resistance (ASR) was observed for such alloys as compared to ferritic stainless steels that form single-layer chromia scales. This drop in resistance was attributed to the MnCr$_2$O$_4$ impeding the ingress of
oxygen and limiting the underlying growth of the chromia scale. We observed a similar phenomenon in the EDXS maps such as Figure 4.6, which show a substantially thinner Cr$_2$O$_3$ scale being formed below the MnCr$_2$O$_4$ outer spinel than in the exposed regions. Stanislawski et al. [22] showed that alloys such as Crofer 22APU, which form outer MnCr$_2$O$_4$ layers, exhibit 60-70% less chromia volatility than pure chromia formers such as Ducrolloy. However, it was also shown that Cr can still diffuse rapidly through the MnCr$_2$O$_4$ thus replenishing the source for evaporation of chromium species. It was concluded that the reduction in chromia volatility for alloys with two-layer chromia/spinel scales was solely due to the lower partial pressure of volatile chromia species that form over MnCr$_2$O$_4$ as compared to that over Cr$_2$O$_3$.

Although MnCr$_2$O$_4$ may be effective at retarding oxidation rates and inhibiting the egress of volatile chromium species, the electrical conductivity at 800 °C is still rather low (0.004-0.08 S/cm [27,79]). It is unclear what effect the substitution of small amounts of Fe into MnCr$_2$O$_4$, as observed in the present study, would have on electrical conductivity. It seems likely that the RL formed on MCO-coated Crofer 22APU has a much higher conductivity than the MnCr$_2$O$_4$ formed on the bare alloy. Wang et al. [78] measured the conductivities of spinels with chemistries similar to the RL reported previously by the current authors [59] and obtained of 22.2 S/cm. We note that the RL reported in our previous work contained a small amount of Fe, while the spinels studied by Wang et al. contained only Mn, Cr and Co; thus additional conductivity measurements are needed to evaluate the properties of the RLs formed on MCO-coated Crofer 22 APU systems.

We note that the RL formed on MCO-coated Crofer 22APU appears to be beneficial in slowing down oxidation kinetics as proposed in the model developed by Chen et al. [48]. The
current work shows that pre-oxidation heat-treatment of Crofer 22 APU not only reduces the parabolic oxidation constant by 3.5x but also promotes the formation of additional MnCr$_2$O$_4$ as compared to the AR samples. Thus, heat treatment of the alloy prior to MCO coating might result in a thicker RL, which would further reduce the oxidation rate for Crofer 22 APU. The combined effects of alloy heat treatment and a protective spinel coating have not yet been studied, but this approach could potentially result in values of $k_g$ over an order of magnitude lower than those for AR bare Crofer 22 APU.
Figure 4.1: Optical micrographs showing etched metallographic sections through coupons of the AR (a,b), HT1h (c,d) and HT4h (e,f) materials; (a), (c) and (e) are coupons before oxidation whereas (b), (d) and (f) are coupons oxidized at 800°C for 750 h.
Figure 4.2: Plot of parabolic weight gain \( (\text{mg}^2 \cdot \text{cm}^{-4}) \) vs. exposure time for samples exposed in static air at 800 °C. The gravimetric rate constants \( (k_g) \) measured from the linear region between 250 h and 750 h were \( 4.82 \times 10^{-8} \text{mg}^2 \cdot \text{cm}^{-4} \cdot \text{s}^{-1} \), \( 2.82 \times 10^{-8} \text{mg}^2 \cdot \text{cm}^{-4} \cdot \text{s}^{-1} \) and \( 1.41 \times 10^{-8} \text{mg}^2 \cdot \text{cm}^{-4} \cdot \text{s}^{-1} \) for the AR, HT1h and HT4h samples, respectively.
Figure 4.3: Plan view BSE SEM images of the oxide scale surface for samples oxidized for 750 h at 800 °C: (a) AR, (b) HT1h and (c) HT4h.
Figure 4.4: XRD data obtained from the surface of samples oxidized for 750 h at 800 °C.
Figure 4.5: TEM data acquired from a FIB-cut cross section through the surface of an AR sample oxidized for 750 h at 800 °C: (a) BF TEM image; (b), (c) and (d) SADPs from regions 1, 2 and 3 in (a), respectively. The single crystal zone axis patterns in (b) and (d) correspond to a cubic spinel phase whereas the spotty ring pattern in (c) is consistent with the corundum structure of $\text{Cr}_2\text{O}_3$. 
Figure 4.6: STEM data acquired from a FIB-cut cross section through the surface of an AR sample oxidized for 750 h at 800 °C. The BF image shows the region analyzed and the X-ray maps show the integrated intensities in 100 eV windows centered on the K \( \bar{\pi} \) energies for each element.

Figure 4.7: BF TEM images acquired from a FIB-cut cross section through the surface of samples oxidized for 750 h at 800 °C: (a) HT1h, (b) HT4h.
Figure 4.8: STEM data acquired from a FIB-cut cross section through the surface of an HT1h sample oxidized for 750 h at 800 °C: (a) BF image; (b) compositional profile obtained from spectra acquired at points along the horizontal line in (a).
Figure 4.9: STEM data acquired from a FIB-cut cross section through the surface of an HT4h sample oxidized for 750 h at 800 °C: (a) BF image; (b) compositional profile obtained from spectra acquired at points along the horizontal line in (a).
Figure 4.10: Bright field TEM image showing internal oxides in an HT4h sample oxidized for 750 h at 800 °C. The inset is an SADP taken from the oxide particle labeled “1”.
Figure 4.11: SE SEM images obtained from an AR sample oxidized for 5 h at 800 °C: (a) morphology of the oxide scale surface; (b) FIB-cut cross-section through the surface.

Figure 4.12: SEM data obtained from the surface of an AR sample oxidized for 5 h at 800 °C. The SE image shows the region analyzed and the X-ray maps show relative intensities.
proportional to the local composition of each element from quantitative analysis of EDXS data at each pixel.

Figure 4.13: SE SEM images obtained from an HT4h sample oxidized for 5 h at 800 °C: (a) morphology of the oxide scale surface; (b) FIB-cut cross-section through the surface.
Figure 4.14: SEM data obtained from the surface of an HT4h sample oxidized for 5 h at 800 °C. The SE image shows the region analyzed and the X-ray maps show relative intensities proportional to the local composition of each element from quantitative analysis of EDXS data at each pixel.

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>Fe</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Cu</th>
<th>Al</th>
<th>S</th>
<th>P</th>
<th>Ti</th>
<th>La</th>
</tr>
</thead>
<tbody>
<tr>
<td>min</td>
<td>20.0</td>
<td></td>
<td>0.30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.03</td>
<td>0.04</td>
</tr>
<tr>
<td>max</td>
<td>24.0</td>
<td>Bal.</td>
<td>0.03</td>
<td>0.80</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
<td>0.02</td>
<td>0.05</td>
<td>0.20</td>
<td>0.20</td>
</tr>
</tbody>
</table>

Table 4.1: Composition of Crofer 22 APU
Chapter 5: Reaction Layer Formation on MCO Coated Crofer

5.1 Introduction/Preamble

Solid Oxide Fuel Cells (SOFCs) have the potential to play an important role in the future of power generation due to their fuel flexibility and high system efficiencies. Recent progress in manufacturing thinner electrolyte layers has enabled SOFC operating temperatures to be reduced from 1000 °C to 600-800 °C. One benefit of this reduced operating temperature is that stack components such as interconnects, which had previously been made of expensive ceramic materials, can now be replaced by metallic components. Metallic interconnects are attractive due to their low cost, high electrical conductivity and high formability which makes them easy to manufacture on a large scale. Most of the interconnect materials currently under consideration are iron- or nickel-based alloys that contain chromium and form a protective, semi-conductive chromia scale as an oxidation product. Unfortunately, exposure of chromia scales in air at elevated temperatures during SOFC operation causes the formation of volatile CrO$_2$(OH)$_2$ and CrO$_3$, leading to poisoning of the cathode materials [21,22,55]. Thus, current SOFC interconnect alloys require protective coatings that suppress the formation of these volatile chromia species [56,57].

The most successful coatings to date have been based on manganese cobaltite ((Mn,Co)$_3$O$_4$ - MCO), which inhibits chromia volatility while simultaneously slowing the oxidation kinetics of the base alloy (e.g.,[81]). The most widely studied MCO composition is Mn$_{1.5}$Co$_{1.5}$O$_4$; it has been shown that coatings with this stoichiometry exhibit two-phase microstructures (comprising cubic MnCo$_2$O$_4$ and tetragonal Mn$_2$CoO$_4$ spinel phases) and electrical conductivities of > 60 S/cm at
800 °C [24, 25]. Such MCO spinel coatings are typically applied as a slurry followed by a two-step (reduction/oxidation) reactive sintering process. However, slurry-processed coatings tend to be rather porous, and there has been a recent push to develop denser coatings by electrodeposition of metallic layers followed by oxidation to form the spinel phases [43, 81, 82]. Other groups have attempted to tailor the MCO chemistry by introducing substitutional cations into the spinel structure to increase the densities and/or electrical conductivities of the coatings [33, 54]. Experimental results from Pacific Northwest National Laboratory (PNNL) have confirmed that low-level (< 1 atomic %) additions of rare earth elements such as cerium to the MCO coating improved the chromia scale adhesion on ferritic stainless steel substrates [26]. This is particularly important for long-term durability as experimental tests indicate that the chromia/alloy interface may be mechanically weaker than the chromia/coating interface [29]. Ce-modified MCO coated stainless steel 441 exhibits an acceptably low and stable area specific resistance (ASR) after >15,000 hours of exposure at 800 °C [83].

A major concern for any such high-temperature coating system is the possibility of reaction layers (RLs) forming between the coating and the alloy or the chromia sub-scale. Since the electrical and mass transport properties of such RLs could be rather different from those of the coating or the sub-scale, RL formation may play a critical role in the degradation of interconnect performance. These issues were discussed in a recent viewpoint paper by Fergus [77], and it was suggested that the most likely outcome was the formation of (Mn,Co,Cr)₃O₄ reaction layers at the chromia / MCO interface. Subsequently, experiments were performed to model these interactions using MCO / Cr₂O₃ diffusion couples with Pt markers at the interface [78]. X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersive X-ray spectrometry (EDXS) were used to analyze the couples after exposure for 24h at 1200°C. It
was found that a (Mn,Co,Cr)$_3$O$_4$ spinel reaction bilayer was formed due to inward diffusion of Mn and Co, and outward diffusion of Cr. These studies also revealed the effects of various transition metal MCO dopants on the rates at which the reaction layers developed. In parallel neutron diffraction studies [84, 85] the details of the site occupancies in (Mn,Co)$_3$O$_4$ and (Mn,Co,Cr)$_3$O$_4$ spinel structures have been investigated.

Although experiments of the type performed by Fergus et al. give a fundamental insight into the processes that can occur in these systems, detailed microstructural and chemical characterization experiments on real reaction layers formed under long-term SOFC operating conditions will be necessary for the development of the future generations of SOFC interconnect coatings. In our work we have studied Haynes 230 and Crofer22 APU alloys coated with Mn$_{1.5}$Co$_{1.5}$O$_4$ and exposed for up to 1000 h at between 700-900 °C. We have previously reported SEM/EDXS evidence for the formation of reaction layers in both systems [48] with the reaction layers formed on Crofer22 APU being thicker than those on Haynes 230. It was proposed that the effects of such layers on the oxidation kinetics could be described using a 3-layer oxidation kinetics model based upon an equivalent circuits approach.

In this paper we present the results of a detailed microstructural investigation on the MCO-coated Crofer22 APU samples from our previous study [48]. These samples were examined in the as-coated condition and after exposure times of 250 and 1000 h at 800 °C. Focused ion beam (FIB) cross-sectioning was used to obtain thin samples for transmission electron microscopy (TEM) studies. The chemistries of the various phases in the samples were determined by EDXS in scanning transmission electron microscopy (STEM) mode. It is shown that the reaction layers are rather different from those reported in the literature with spinels forming both at the
alloy/chromia and chromia/MCO interfaces. These data are used to infer the mechanisms by which the reaction layers form, and the likely effects of these layers on the overall lifetime and performance of the SOFC stacks are discussed.

5.2 Results

5.2.1 Development of interfacial layers/reaction products

The development of the interfacial reaction products was revealed by comparing STEM imaging and spectrometry data from the as-coated, 250 h and 1000 h samples: representative data are presented in Figures 5.1, 5.2 and 5.3, respectively. Figure 5.1(a) is an ADF image obtained from the FIB-cut cross-section of the as-coated sample with the alloy on the left-hand side of the image and the MCO coating on the right. Figure 5.1(b) is a compositional profile determined from EDXS measurements obtained along the bright horizontal line indicated in Figure 5.1(a). Spectra were acquired using a 10nm spot size at 10nm intervals along the line with a 3s integration time at each point. Compositions were extracted from each spectrum using a standard-less quantification of integrated intensities in each of the corresponding K peaks based upon the thin film approximation. The first 2µm of this profile show a high constant Fe content of about 82 wt.%, with the balance being comprised of Cr, corresponding to the Crofer22 APU. There is then a band approximately 700 nm wide containing approximately 66 wt.% Cr and 33 wt.% O, as expected for a Cr₂O₃ scale (stoichiometric chromia contains 68 wt.% Cr and 32 wt.% O). Beyond this, there is a band around 3µm thick which comprises a mixture of O, Cr, Mn and Co in varying proportions. We designate this layer the Reaction Layer (RL). On the left is a region of near constant O content with complementary variations in Mn and Co; this is consistent
with what one would expect for an MCO coating with average composition \( \text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4 \), which should give roughly equal proportions of \( \text{Mn}_2\text{CoO}_4 \) and \( \text{MnCo}_2\text{O}_4 \) phases. There is also a low Fe content (2-6 wt. \%) present in the RL and MCO layers. We note that while these four layers/regions are broadly representative of the data obtained from the as-coated samples, the thicknesses of the chromia scale and the RL varied significantly with location along the interface.

The distributions of the various elements in the RL were revealed more clearly in X-ray mapping experiments and a selection of these data is shown in Figures 5.1 (c)-(e), for Cr, Co and Mn, respectively. These maps were obtained from the region delineated by the 3.25 x 2.6 \( \mu \text{m} \) box marked on the ADF STEM image (Figure 5.1(a)) and they are shown at the same scale. Each map corresponds to a grid of 256 x 200 measurements of the counts within a 100 eV window centered on the K\( \alpha_1 \) energy for that element. The data were acquired by scanning the region 2048 times with a dwell time of 0.2 ms per measurement for a total acquisition time of around 5.8 h corresponding to just over 0.4 s per pixel. The darker region in the upper left corner of the Cr map is the edge of the Crofer22 APU substrate and the bright band down the left-hand edge of this map corresponds to the chromia scale. Just beyond this is a broader region that is enriched in Cr and Co but not Mn, and on the right-hand side is a region enriched in Co and Mn but not Cr: this latter region corresponds to the MCO. The interfaces between the three oxide regions are very rough, particularly for the Cr/Co-rich and MCO regions wherein the former appears to penetrate into the latter. Indeed there are some thin Cr/Co-rich bands around MCO grains/domains extending to the right-hand side of the mapped region. It is presumably this complex distribution of the Cr/Co-rich and MCO regions that leads to the compositional variations observed in the RL in Figure 5.1(b).
A more clearly defined structure comprising layers of more consistent thickness was evident in the STEM data from the 250 h sample (Figure 5.2). The ADF image in Figure 5.2(a) and the compositional profile in Figure 5.2(b) were obtained under the same conditions as those for the as-coated sample in Figure 5.1. The chromia scale is a little thicker (around 1µm), but the reaction layer is thinner (1.5-2 µm) in this sample than in the as-coated sample. Here again, there are significant fluctuations in the Co, Mn and O contents of the RL, but the Cr content seems to decay steadily with distance from the chromia/RL interface. The Fe contents of the RL and MCO are also lower (1-3 wt. %) in this sample. In addition to these features, we note that there were Ti-rich particles that range from 100-400 nm in diameter within the Crofer22 APU substrate; these can be seen as bright equiaxed features in Figure 5.2(a): two examples of such features are indicated by arrows in the figure. There are also occasional well-defined pockets of Cr- and Mn-rich sub-scale (SS) oxide at the boundary between the alloy and the chromia scale, and two examples of such pockets are labeled SS in Figure 5.2(a).

The corresponding STEM data from the 1000 h sample are shown in Figure 5.3. Although the thickness of the chromia scale is similar to that of the 250 h sample at around 1.25 µm, the thickness of the RL is much larger, and it appears that the RL has almost completely consumed the MCO coating in this sample. The transition in Cr content from the chromia scale to the RL is much more abrupt, but thereafter the Cr profile is shallower. Indeed over the first 4 µm of the RL, the variations in the Co, Cr, Mn and O contents are rather gradual with no abrupt compositional changes such as those observed in the RL for the as-coated and 250 h samples. Here again, Ti-rich particles were observed within the alloy below the chromia scale, and well-defined Cr- and Mn-rich SS pockets were observed at the alloy/chromia interface.
The grain structure of the microstructural regions in these samples was revealed more clearly from diffraction contrast effects in axial bright field (BF) TEM images obtained from the FIB-cut samples. One example of such a BF image is shown in Figure 5.4, which was obtained from the 1000 h sample. The regions corresponding to the alloy substrate, the SS pockets, the Cr$_2$O$_3$ scale and the RL are indicated. Such images were used to obtain measurements of the grain sizes in the chromia scale and RL for each sample, and the data are presented in Table 5.1. These data show that the mean grain sizes in the RL exceed those for the chromia scale by a factor of 3-4 and that these values increase with increasing oxidation time. Too few SS pockets were observed for meaningful mean grain diameters to be extracted from these regions, but it is clear from Figure 5.4 that the grains are substantially larger than those in the RL.

5.2.2 Phase Identification

The phases formed by the interaction of the Crofer22 APU and the MCO coating were identified using a combination of SADPs and EDXS spot analyses on the FIB-cut cross sections. Examples of the TEM data obtained for the phase identification are shown in Figure 5.5: in each case a BF TEM image is presented together with the corresponding SADP. We note that all of the data shown in Figure 5.5 were obtained from the 1000 h sample, which has the largest grain size and gave the most easily interpretable SADPs and EDXS data. No data is presented for the BCC matrix phase of the alloy, or for the cubic MnCo$_2$O$_4$ and tetragonal Mn$_2$CoO$_4$ phases of the MCO coating since these are well established. The data from the small Ti-rich particles in the alloy adjacent to the chromia scale in the 250 h and 1000 h samples have also been omitted from this figure. These particles contained Ti and O at an atomic ratio of approximately 1:2 with up to
5 at. % Cr, and the SADPs indicated that each particle is a single crystal. Although the measured chemistry was consistent with the particles being Cr-doped TiO$_2$, the zone axis SADPs were not consistent with any of the three known polymorphs of TiO$_2$ (anatase, brookite or rutile).

Figure 5.5(a) is a BF TEM image obtained from a SS pocket at the interface with the Crofer22 APU substrate. This region is clearly distinguished from the darker alloy region on the left-hand side of the image and the fine-grained chromia scale on the right. The corresponding SADP (Figure 5.5(b)) is consistent with this being a phase with a face-centered cubic (FCC) lattice (due to the systematic absences) and a lattice parameter of 0.845 nm; the SADP is indexed on this basis and corresponds to a [112] zone axis pattern. The EDXS data from this pocket showed that the SS contained only Mn, Cr and O at an atomic ratio of exactly 1:2:4. The same result was obtained from another pocket in this sample and from SS pockets in the 250 h sample, indicating that the SS pockets consist of stoichiometric grains of the cubic spinel phase MnCr$_2$O$_4$ ($a_0 = 0.844$ nm [73]) in both samples.

Figures 5.5(c) and (d) are a BF TEM image and a corresponding SADP from the chromia layer. The grains were too fine to obtain single crystal zone axis SADPs but all of the spots in Figure 5.5(d) lie on the rings expected for Cr$_2$O$_3$ with the corundum structure ($a_0 = 0.496$ nm, $c_0 = 1.359$ nm), as anticipated from the EDXS line-scan data (Figure 5.3(b)). The EDXS point analyses performed are consistent with this being stoichiometric Cr$_2$O$_3$; the only other species present are Ti and Fe at a total impurity content of less than 0.5 atomic %.

Figure 5.5(e) is a BF TEM image showing a large grain in the RL. The corresponding zone axis SADPs were consistent with this being a grain of a cubic spinel phase with a lattice parameter of 0.845 nm, i.e. the same as for the SS MnCr$_2$O$_4$. One example is shown in Figure
5.5(f), which is a [111] zone axis pattern. The EDXS data obtained from this region show that the RL grains contain Mn, Co, Cr and Fe; these cations are not present in simple ratios, and the measured concentrations correspond to a spinel composition of \( \text{Mn}_{1.38}\text{Co}_{0.84}\text{Cr}_{0.54}\text{Fe}_{0.24}\text{O}_4 \). There was very little evidence for any grain-to-grain or through-thickness variation in spinel composition from the EDXS data. It is important to note that while we have treated the RL as a cubic spinel in this analysis, there is some subtle splitting of the 220-type reflections in the SADP and very fine (≈5nm wide) periodic contrast within the RL grains in the BF TEM image. These features may indicate the onset of a transformation from the cubic phase to a lower-symmetry phase upon cooling.

The diffraction data obtained from the RL grains in the 250 h and as-coated samples were also consistent with a cubic spinel phase, although the lattice parameters were slightly smaller at 0.826 and 0.838 nm, respectively. The mean compositions of these RL grains in the scanned areas were obtained from the EDXS data and converted to a spinel formulation in the same manner as for the 1000 h sample; the values obtained were \( \text{Mn}_{0.79}\text{Co}_{1.38}\text{Cr}_{0.80}\text{Fe}_{0.03}\text{O}_4 \) and \( \text{Mn}_{0.33}\text{Co}_{0.94}\text{Cr}_{1.57}\text{Fe}_{0.16}\text{O}_4 \), respectively. We note that there was far more grain-to-grain variation in spinel composition in these cases, particularly for the as-coated sample.

### 5.3 Discussion

#### 5.3.1 Comparison with previous microstructural studies

The main microstructural features observed in the present work are broadly consistent with those reported in previous studies on MCO-coated Crofer22 APU and on some related systems.
Firstly, there is the formation of a continuous chromia scale between the alloy and the MCO coating. This is consistent with previous studies on MCO-coated ferritic stainless steels (e.g. [25]) including Crofer22 APU, and indeed it is the inhibition of chromia growth and/or confinement of chromia to the alloy/coating interface that is the primary purpose of the coating.

Secondly, there is the presence of the oxide RL corresponding to the interaction of the chromia and the MCO coating. This RL was detected in our previous studies on MCO-coated Crofer22 APU [48], and is anticipated on the basis of results from chromia-MCO diffusion couples [78]. We note however that other studies on MCO-coated Crofer22 APU have reported no incorporation of Cr into the MCO layer even after extended exposure at 800°C [26]. One possible explanation for this discrepancy is the difference between the spatial resolution for chemical microanalysis in the SEM used in these studies and that in the TEM used here. The spatial resolution of EDXS-based microanalysis in SEM is typically no better than 1µm, and so it is possible that a narrow RL might not be detected by this technique.

Similar arguments can be used to explain the apparent differences between the MCO compositional profiles presented here and those reported elsewhere. Profiles obtained from MCO using EDXS in SEM typically show a fairly constant composition (e.g. [25, 26, 48]), whereas XRD data show clearly that the Mn$_{1.5}$Co$_{1.5}$O$_4$ composition comprises a mixture of cubic MnCo$_2$O$_4$ and tetragonal Mn$_2$CoO$_4$ spinel phases [25]. The data in Figures 5.1(b) and 5.2(b) show clearly that the grains/domains of the phases are less than 1µm in diameter; thus an EDXS measurement of the composition in an SEM will sample both phases giving an average MCO composition, whereas the TEM has a microanalytical resolution of around 20 nm under the conditions used here and the constituent phases are resolved clearly.
The main differences between the observations presented here and those in the literature relate to the features on the alloy side of the chromia scale and to the character of the RL. In the 250 h and 1000 h samples we observed SS pockets at the alloy/chromia interface and internal oxides within the Crofer22 APU below the chromia. The SS pockets were identified unambiguously as stoichiometric cubic MnCr$_2$O$_4$ spinel. The internal oxides had a chemistry corresponding to Cr-doped TiO$_2$, although the diffraction data were not consistent with any known polymorph of titania. There have been no previous reports of such SS pockets or internal oxides for MCO-coated samples. We note, however, that MnCr$_2$O$_4$ is the phase that forms on the exposed surface of uncoated Crofer22 APU during elevated temperature oxidation in air [60]. Moreover, there have been reports of “Mn-rich intrusions” at the alloy/chromia interface and “TiO$_2$ precipitates” in cross-sectional SEM studies of a different ferritic stainless steel with a very similar composition after oxidation of uncoated samples for 6000 h at 800°C in air [73], although no details of the phase identification were provided. The formation mechanism of these MnCr$_2$O$_4$ pockets is not yet well understood; further experiments on uncoated systems are needed in order to ascertain whether this is an inherent feature of the alloy or a reaction product formed between the alloy and coating.

More significantly, the observations presented here on the RL show dramatic changes in the morphology and character of the spinel, and these findings differ significantly from what is reported elsewhere. Recent work on MCO/chromia diffusion couples [78] has shown that diffusion of Mn and Co into the Cr$_2$O$_3$ and concurrent Cr diffusion into the MCO results in a spinel reaction bilayer with (Mn,Co,Cr)$_3$O$_4$ on the MCO side and (Mn,Co)Cr$_2$O$_4$ on the chromia side. In our samples we observe essentially only a single spinel RL between the MCO and the chromia. In the as-coated sample this RL is roughly 3µm thick, penetrates into the MCO coating.
above, and is enriched in both Cr and Co (Mn:Co:Cr ≈ 1:3:5). The 250 h sample exhibits a more compact (1.5-2.0 μm thick) well-defined RL that is Co-rich (Mn:Co:Cr ≈ 4:7:4). In the 1000 h sample, however, the RL is thicker (>4μm) and is Mn-rich (Mn:Co:Cr ≈ 7:4:3). Possible ways in which this complex sequence of RL spinels could develop are discussed below.

5.3.2 Microstructural development during coating and high temperature exposure

When considering the development of the coating microstructure, it is informative to compare the way in which the Cr distribution changes. Figure 5.6 is an overlay of the Cr profiles for the as-coated, 250 h and 1000 h samples extracted from Figures 5.1(b), 5.2(b) and 5.3(b), respectively. For the purposes of comparing the profiles, the position of the abrupt Crofer22 APU/chromia interface was identified as the point where the Fe and Cr contents are equal in each case, and the Cr profiles were then displaced to x=0.5μm. It is important to note that this is the final position of the Crofer22 APU/chromia interface, not the original position of the Crofer22 APU substrate surface, although the two positions will not vary dramatically because the overall oxidation rate of this coated system is very low. Two important features emerge from this figure. Firstly, there is very little thickening of the chromia scale: the chromia is around 0.7 μm in the as-coated sample, and this rises to about 1μm in the 250 h sample and 1.25μm in the 1000 h sample. Secondly, the Cr profile in the RL shows a complex variation with exposure time. In the as-coated sample the Co/Cr-rich spinel RL extends 3-4 μm into the coating, although the profile is very uneven due to porosity and intergrowth of the RL spinel with the MCO as discussed in section 3. After 250 h exposure, however, this spinel is replaced by a much thinner (1.5 μm) RL with a lower Cr content. After 1000 h, the spinel RL has thickened to >4μm. These data seem to
imply that the Cr initially diffuses outwards during the coating process, then inwards during the initial exposure, then outwards again during more extended exposure.

To explain this remarkable sequence of Cr fluxes it is necessary to recall that the as-coated state is the net result of three processing steps: application of the MCO slurry to the bare Crofer22 APU substrate, reduction in a Ar+H₂+H₂O mixture at 850°C, and then re-oxidation in air at the same temperature. Yang et al. showed that the reduction step converts the MCO to a mixture of manganous oxide (MnO) and metallic Co. It is the presence of metallic Co between the MnO grains that gives the sintering and densification of the coating during the reduction step, but this could also facilitate the outward diffusion of Fe and Cr, both of which exhibit extensive solid solubility in FCC Co at the reduction temperature. Upon re-oxidation, however, one would expect the mixture of metallic Co + MnO phase to convert back to MCO (or some closely related spinels) with the Mn displacing Cr and Fe and causing a reversal of the flux for these species. Once the equilibrium Mn concentration had been (re) established in the MCO, however, Cr and Fe might once again diffuse outwards. Using this as a working hypothesis, one could envisage the microstructural development as occurring by the processes depicted in Figure 5.7 and described below.

Firstly, the MCO slurry is applied to the Crofer22 APU substrate and dried at 100°C giving a porous friable green coating of MCO particles held together only by a small volume fraction of polymer binder (Figure 5.7(a)). The binder is eliminated during ramping to the reduction temperature, and the MCO particles are then reduced to MnO+Co in the Ar+H₂+H₂O mixture. We can then account for the as-coated microstructure if there is some preferential redistribution of Co to the alloy/coating interface so that the alloy is in contact with the metallic FCC Co phase.
As such, one might expect diffusion of Cr and Fe into the FCC Co-rich metal at the interface (Figure 5.7(b)). This process is presumably more rapid for Cr than for Fe due to the differences in the diffusion coefficients. Moreover, given the extensive solubility of Mn in Co at the reduction temperature, it seems likely that the metallic FCC phase will also contain some Mn. During the subsequent re-oxidation, one might expect the reverse processes to occur, i.e. reaction of MnO+Co to form MCO and the concurrent diffusion of Cr and Fe back towards the substrate. If, however, the oxidation front advances more rapidly than the Cr and Fe can diffuse (as one might expect since the diffusivity of O in Co is far higher than that of Cr or Fe), then the cation content of the oxide at the coating/alloy interface would correspond more closely to that of the metallic layer formed during reduction than to that of the starting MCO powder. One would also expect the formation of a compact chromia layer at this interface. These processes would account for the formation of a rather thick Co/Cr-rich and Mn-lean spinel RL between the chromia scale and the MCO (Figure 5.7(c)) as observed experimentally for the as-coated sample (Figure 5.1). Since the RL in this condition is Mn-lean, the adjacent MCO must be Mn-rich with more Mn$_2$CoO$_4$ than MnCo$_2$O$_4$. If these MCO phases are more stable than the Co/Cr-rich spinel in the RL then during subsequent extended exposures one might expect inward Mn diffusion. The Cr displaced by the Mn could be incorporated into the chromia scale giving a much narrower Cr profile (Figure 5.7(d)) as observed for the 250 h sample (Figure 5.2). Once the Co/Cr-rich spinel has been consumed, subsequent reactions may be mediated by the chromia scale in the manner discussed by Fergus et al. [77]-[78] wherein the chromia is simultaneously consuming the alloy while it is being consumed by the diffusion of Mn and Co to form a reaction layer (Figure 5.7(e)). This is consistent with our results, which show that the chromia scale thickness is not increasing significantly over the time periods considered here. The consumption of the chromia
at the interface with the coating would result in the re-incorporation of Cr into the spinel phases establishing a Cr-modified RL as observed for the 1000 h sample (Figure 5.3). The absence of any significant compositional fluctuations in this layer (as compared to the co-ordinated modulations in Co and Mn in the Cr-free MCO) suggests that the Cr in the RL is stabilizing one of these spinel phases over the other.

5.3.3 Implications for oxidation kinetics and fuel cell performance

To date, most of the SOFC interconnect literature cites the chromia scale thickness as being the main contributor to the development of ohmic losses with exposure time. The current work clearly shows that (Mn,Co,Cr,Fe)$_3$O$_4$ reaction layers that form even after 1000 hours constitute the majority of the interface. Therefore it is not just the conductivity of the chromia scale, but also the conductivity of the spinel reaction layers that form that are critical to achieving long term durability at SOFC operating temperatures. Electrical conductivity values of varying compositions of (Mn,Co,Cr)$_3$O$_4$ have been reported by Wang et. al. [78] and indicate that adding Cr to the MCO spinel structure decreases the conductivity. Spinel pellets of Mn$_{1.25}$Co$_{1.25}$Cr$_{0.5}$O$_4$, MnCoCrO$_4$ and Mn$_{0.4}$Co$_{0.6}$Cr$_2$O$_4$ measured at 800 °C had electrical conductivity values of 22.2 S/cm, 2.3 S/cm and 0.009 S/cm respectively. Chromia conductivity is dominated by defects and measured values vary widely (0.006 - 0.16 S/cm). The composition of the spinel reaction layer reported here for the 1000h sample is similar to the Mn$_{1.25}$Co$_{1.25}$Cr$_{0.5}$O$_4$ case considered by Wang et. al. [78] (assuming that Fe substitutes for Co). Thus we might expect the conductivity of this reaction layer to be somewhat lower than that of
the starting MCO composition, but still at least two orders of magnitude higher than that of the chromia scale.

Previous work by the current authors proposed an equivalent circuit model to explain differences in weight gain observed between MCO coated Ni-base alloys and MCO coated ferritic stainless steels. The models suggest that the thicker reaction layer formed on the ferritic stainless steels may act as an oxygen diffusion barrier, which slows down the chromia subscale growth. MCO coatings on H230 Ni-base alloys were not as effective at slowing oxidation of the underlying alloy which is presumably due to the much thinner reaction layers formed on these alloys [48]. Thus, it appears as though the reaction layer may have a beneficial effect in terms of limiting chromia scale formation, but does so at the expense of electrical conductivity of the coating. It is expected that after long exposure times, as will be seen in SOFC applications, the MCO coating will be entirely consumed and replaced by a $(\text{Mn,Co,Cr,Fe})_3\text{O}_4$ reaction layer

Subscale spinel pockets of MnCr$_2$O$_4$ observed in the current work must also be considered a potential degradation mechanism for fuel cell performance for this particular alloy/coating system. The literature suggests that the MnCr$_2$O$_4$ spinel has an electrical conductivity of 0.004 S/cm at 800 °C [79]. This phase is therefore highly undesirable from an electrical conductivity standpoint and could potentially contribute to ohmic losses in MCO-coated Crofer22 APU interconnects.
Figure 5.1: (a) BF STEM image acquired from a FIB-cut thin cross-section through the as-coated sample. (b) Compositional profile obtained from spectra acquired at points along the horizontal line in (a). (c)-(d) X-ray maps obtained from the area indicated by the dotted box in (a) using the integrated intensities in 100 eV windows centered on the K\(\alpha_1\) energies for: (c) Cr, (d) Co and (e) Mn.
Figure 5.2: STEM data acquired from a cross-section through the 250 h sample: (a) BF image; (b) compositional profile obtained from spectra acquired at points along the horizontal line in (a).
Figure 5.3: STEM data acquired from a cross-section through the 1000 h sample: (a) BF image; (b) compositional profile obtained from spectra acquired at points along the horizontal line in (a).
Figure 5.4: BF TEM acquired from a cross-section through the 1000 h sample. “SS” denotes pockets of subscale spinel observed between the alloy and chromia scale.
Figure 5.5: TEM data acquired from the following microstructural layers in a cross-section through the 1000 h sample: (a) and (b) SS pocket, (c) and (d) chromia scale, (e) and (f) RL. The SADPs in (b), (d) and (f) were obtained from the regions in the center of the areas shown in the BF TEM images (a), (c) and (e), respectively.
Figure 5.6: Overlay of the Cr compositional profiles from Figures 1(b), 2(b) and 3(b). In each case these are displaced laterally to give the alloy/chromia interface at 0.5µm for ease of comparison.
Figure 5.7: Schematic diagrams showing the development of microstructural layers and the senses of the associated diffusive fluxes during: (a) application of the MCO slurry; (b) reduction in Ar+H$_2$+H$_2$O; (c) re-oxidation in air; (d) the initial stages of long-term oxidation; (e) the later stages of long-term oxidation. Oxide phases are shaded grey, metallic phases are white and the black regions in (a) are pores.
Table 5.1: Grain sizes measured from TEM cross-section samples for the chromia scale and the (Mn,Co,Cr,Fe)$_3$O$_4$ spinel RL.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chromia Grain Sizes (nm)</th>
<th>RL Spinel Grain Sizes (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Range</td>
<td>Mean</td>
</tr>
<tr>
<td>As-Coated</td>
<td>35-102</td>
<td>72</td>
</tr>
<tr>
<td>250 h</td>
<td>35-213</td>
<td>103</td>
</tr>
<tr>
<td>1000 h</td>
<td>42-467</td>
<td>163</td>
</tr>
</tbody>
</table>
Chapter 6: Oxidation and Reaction Layer Formation on Haynes 230

6.1 Introduction/Preamble

Solid Oxide Fuel Cells (SOFCs) are a key technology for future stationary power generation. The main technical challenges for SOFCs are the limited long-term durability of the various stack components and the high cost of the materials from which they are produced. Recently, metallic interconnects have been favored over their ceramic counterparts because the alloys used are significantly more formable and less expensive. The alloys that have received most attention for interconnect applications are Fe-Cr- and Ni-Cr-based systems that form chromia scales upon oxidation. There are three main problems that can occur with such alloys. Firstly, exposed chromia scales can form volatile species such as CrO$_2$(OH)$_2$ and CrO$_3$ at SOFC operating temperatures [22,13]. These gaseous species can condense at the triple phase boundaries on the cathode and “poison” the cell by decreasing the number of available sites for the oxygen reduction reaction [87]. Secondly, the oxidation rates of the alloys are too high to meet current performance targets. The Ni-Cr alloys are superior to the Fe-Cr alloys in this regard with parabolic oxidation rate constants, $k_g$, 1-2 orders of magnitude lower [9], but even the best Ni-based alloys form excessively thick chromia scales after long-term exposure leading to scale spallation and an unacceptably high increase in ohmic resistance [30]. Protective coatings are currently required for both Fe- and Ni-based chromia-forming alloys to mitigate both the oxidation kinetics and the release of volatile chromia species, [56, 57]. The third issue that can affect metallic interconnects is delamination due to coefficient of thermal expansion (CTE) mismatch between the alloy and the ceramic cell materials. This is less of a concern for Fe-Cr alloys which have CTE values of $10-12 \times 10^{-6}$ K$^{-1}$ [88] than for Ni-base alloys which have CTE...
values of $14.9-15.2 \times 10^{-6} \text{K}^{-1}$ from room temperature to 800° C [14, 89]. While CTE mismatch is a potential issue for rapid thermal cycling of Ni-base alloy interconnects, it has been shown that this effect can be mitigated by using an open corrugated design [90] or a clad multilayer composite [91].

The Ni-based alloy that has attracted the most attention is Haynes 230 (H230), which exhibits good high-temperature strength, corrosion resistance and thermal stability. The chemical composition for H230 is given in Table 6.1 [15]; the alloy exhibits an austenitic structure [89] and is both solid-solution- and carbide-strengthened [92]. The two main carbide phases in H230 are $W_6C$ in the form of stringers and fine $\text{Cr}_23\text{C}_6$ precipitates at the alloy grain boundaries; these carbide phases play a significant role in strengthening the alloy at elevated temperatures [93]. Bare H230 has been reported in the literature to form a two-layer oxide scale with an inner $\text{Cr}_2\text{O}_3$ layer and an outer $(\text{MnCr})_3\text{O}_4$ spinel scale [52,72,94,95] with internal $\text{Al}_2\text{O}_3$ oxides forming in the alloy below the chromia scale [92]. England and Virkar reported a $k_g$ value of $1.29 \times 10^{-15}$ $\text{g}^2\text{cm}^{-4}\text{s}^{-1}$ for H230 oxidized at 800° C in air, and they attributed the slow oxidation kinetics of H230 to the formation of a MnCr$_2$O$_4$ outer spinel layer [52]. It is well established that the equilibrium partial pressure of oxygen needed to oxidize chromium is $10^{-28}$ atm while that required for oxidation of Mn is only $10^{-30}$ atm (e.g. [52]). In addition, the diffusion of Mn cations through chromia is 1-2 orders of magnitude faster than diffusion of Cr through chromia [69, 70]. Thus, even a small amount of Mn in the starting alloy composition (0.5 wt.% for H230) results in the formation of an outer Mn-Cr spinel phase. However, previous work on MnCr$_2$O$_4$-forming Fe-Cr alloys showed that the formation of the outer spinel phase does not eliminate chromia evaporation from the surface, but instead serves to lower the equilibrium partial pressure
of volatile chromia species [22]. As such, the majority of the recent work on H230 has focused on spinel- or perovskite-coated systems.

In a previous report by the present authors, preliminary results were presented on the effects of Mn$_{1.5}$Cr$_{1.5}$O$_4$ (MCO) coating on the oxidation behavior of both H230 and the ferritic stainless steel Crofer 22 APU. It was observed that while the MCO was quite effective at inhibiting the oxidation of the Crofer 22 APU, the same coating had little or no retarding effect on the oxidation kinetics of H230 [48]. In subsequent work a combination of focused ion beam (FIB) sectioning and electron microscopy techniques was used to reveal the details of the oxide scale microstructures for uncoated and MCO-coated Crofer 22 APU [59,96]. It was found that the uncoated Crofer also formed a two-layer chromia + MnCr$_2$O$_4$ scale, and that heat treatment prior to oxidation resulted in slower oxidation kinetics and an increase in the proportion of the outer MnCr$_2$O$_4$ spinel layer [59]. The MCO-coated Crofer also exhibited slower oxidation kinetics [48], and this was associated with the formation of a complex series of (Mn,Co,Cr,Fe)$_3$O$_4$ spinel reaction layers between the coating and Crofer substrate [96]. In this paper, we describe a study using similar techniques to evaluate the microstructures in the oxide scales formed on uncoated and MCO-coated H230. It is shown that the oxide scale chemistry and morphology formed on bare H230 leads to a dramatically thinner RL compared to the RL formed on MCO coated Crofer 22 APU. It has been previously shown by the current authors that the thickness of the RL layer formed may have a major impact on the effectiveness of the coating to prevent further oxidation of the interconnect alloy. Detailed microstructure and chemistry data is presented for the RL formed on MCO-coated H230 and implications for long-term SOFC performance are discussed.
6.2 Results

6.2.1 Oxidation and Scale Development of Bare H230

The thermogravimetric data obtained from the uncoated H230 alloy coupons oxidized at 800 °C are shown in Figure 6.1. These are plotted as $(\Delta w/SA)^2$ vs. time, where $\Delta w$ is the change in weight and SA is the surface area of the coupon, so that the slope of the curve $(8.8 \times 10^{-9} \text{mg}^2\text{cm}^{-4}\text{s}^{-1})$ is the parabolic rate constant, $k_g$. SEM images showing the morphology of the oxide scale formed after 1000 h exposure are presented in Figure 6.2. Figure 6.2(a) is a 2 kV backscattered electron image of the oxide scale in plan view showing large faceted features surrounded by finer granular regions. Secondary electron images such as Figure 6.2(b) obtained with the sample tilted at 52° to the electron beam revealed that the large faceted features adopt a tabular morphology.

The character of the oxide scale formed on the bare H230 was investigated by preparing a cross-sectional TEM sample through the alloy/scale interface using FIB; representative STEM and TEM data obtained from this sample are presented in Figures 6.3 and 6.4, respectively. Figure 6.3(a) is a bright field (BF) STEM image with the alloy on the left and the oxide scale on the right. Figure 6.3(b) is a compositional profile determined from EDXS measurements obtained along the bright horizontal line indicated in Figure 6.3(a). Spectra were acquired using a 10nm spot size at 10nm intervals along the line with a 3s integration time at each point. Compositions were extracted from each spectrum using a standard-less quantification of integrated intensities in each of the corresponding K peaks based upon the thin film approximation. The chemical profiles can be broken down into three distinct regions. The first 1 μm is the base alloy, which varies in composition from 60 wt.% Ni, 25 wt.% W and 15 wt.% Cr at the start of the linescan to 50 wt.% Ni, 35 wt.% W and 10 wt.% Cr just below the chromia
scale. We note that this entire region represents a W-rich, Cr-depleted zone since the starting 
base alloy composition is 57 wt.% Ni, 14 wt.% W and 22 wt. % Cr. The next 700 nm of the 
linescan is a chromia layer with a measured composition of 60 wt.% Cr and 40 wt.% O. The 
difference between this measured composition and the value of 68 wt.% Cr, 32 wt.% O expected 
for stoichiometric Cr$_2$O$_3$ may be due to uncertainties in the measured O content because of 
overlap between the O K peak at 523 eV and the Cr L\_{\Pi} peak at 571 eV. The 300 nm thick 
region on the right has a composition of 45 wt.% Cr, 25 wt.% Mn and 30 wt.% O, which is 
consistent with that expected for a MnCr$_2$O$_4$ spinel (stoichiometric composition - 46.7 wt.% Cr, 
24.6 wt.% Mn and 28.8 wt.% O).

The phases present in these layers were confirmed by imaging, diffraction and 
spectrometry experiments in TEM mode. Figure 6.4(a) is a many-beam BF TEM image of the 
alloy/scale interface with the alloy on the left, the scale on the right, and the boundaries between 
the three microstructural layers marked with white lines. Such images reveal that these 
boundaries are abrupt but rather rough. There are light particles with diameters of up to 400nm 
embedded within the alloy below the scale interface. EDXS analysis indicates that these particles 
are probably Al$_2$O$_3$ internal oxides, although it was not possible to obtain unambiguous selected 
area diffraction patterns (SADPs) from these features because of interference from the 
surrounding alloy matrix. Figure 6.4(b) is an SADP obtained from the region marked “1” in 
Figure 6.4(a) and the diameters of all of the rings in this pattern correspond to those expected for 
Cr$_2$O$_3$ with the corundum structure ($a_0 = 0.496$ nm, $c_0 = 1.359$ nm). Similarly, Figure 6.4(c) is an 
SADP taken from the region marked “2” in Figure 6.4(a) and this corresponds to a [\bar{1}12] zone 
axis pattern for the MnCr$_2$O$_4$ spinel ($a_0 = 0.844$ nm).
6.2.2 Microstructure and Morphology of MCO Coated H230

The MCO coating was examined after each stage of the reactive sintering process to investigate the way in which the coating microstructure develops. Figure 6.5 is a selection of images from an EDXS mapping experiment performed on a cross-sectional sample through a slurry-coated coupon that had been subjected to the reduction process but not subsequently re-oxidized. This figure includes: a BSE image of the area analyzed, a series of EDXS maps, and an overlay of these maps to show the relative distributions of the elements more clearly. The maps represent the integrated intensities in 100 eV windows centered on the O K, the Co, Mn, Cr and Ni K\textsubscript{\textalpha}, and the W L\textsubscript{\textalpha} peaks (after deconvolution for overlap where appropriate) for 512 \times 400 spectra acquired over an area of 67 \times 59.5 \, \mu m with a dwell time of 3 ms per point. The top half of the area corresponds to the reduced coating and the bottom half is the alloy substrate. The Co and Mn maps reveal a clear phase separation within the coating. Moreover, by comparing these maps with the O map it can be seen that the Co is reduced to a greater extent than the Mn. The O map also shows an extremely thin O-rich layer between the alloy substrate and the coating. A similar thin layer is also observed in the Cr map, indicating that there is some initial oxidation of the alloy surface to form chromia during the coating reduction process. The Cr map also shows localized Cr-rich regions within the H230 substrate; these are presumably the Cr\textsubscript{23}C\textsubscript{6} carbides which are known to form at the grain boundaries this alloy [93]. The W map reveals other precipitates arranged as “stringers” parallel to the substrate surface; the distribution of these features is consistent with that expected for the primary W\textsubscript{6}C phase in H230. Aside from these features, the Ni, W and Cr maps show uniform background intensity in the alloy consistent with the alloy matrix being a homogeneous solid solution of these elements.
The extent of densification was revealed most clearly in BSE SEM images such as Figures 6.6(a) and (b), which were obtained from cross-sections through coated coupons after the reduction step (i.e. as for Figure 6.5) and the re-oxidation step respectively. The reduced coating is highly porous, and appears to have lifted away from the substrate during mounting in epoxy. The coating on the re-oxidized sample is rather denser and exhibits a level of porosity that is typical of slurry-based spinel coatings.

To reveal the extent of any interactions between the alloy substrate and MCO coating, FIB cut cross-sections were prepared for TEM analysis from the alloy/coating interfaces in the samples shown in Figure 6.7. None of the cross-sections from the reduced sample survived the milling process due to the high level of porosity, but a useable cross-section was obtained from the re-oxidized sample. Figure 6.7 comprises: (a) a BF STEM image obtained from this cross-section, and (b) a compositional profile acquired along the line indicated in (a) using EDXS under the same conditions as those for Figure 6.3(b). There are four distinct regions in the chemical profile. On the left is a 200 nm thick region, whose chemistry is broadly consistent with that of the base alloy although in this near-surface region the Ni and Cr contents are lower, and the W content is higher than expected for the bulk of the alloy (approximately 45, 12 % and 25 wt.%, respectively c.f. 57, 22 and 14 wt.% respectively in the alloy specification). The next 200 nm corresponds to a Cr$_2$O$_3$ layer, although here again the measured Cr:O ratio deviates somewhat from that expected for stoichiometric chromia. The next 350 nm is what we have termed the reaction layer (RL), and this consists of varying mixtures of Cr, Mn, Co and a small amount of W. The measured oxygen content throughout this region is approximately 30 wt.%. The last 200 nm of the linescan exhibits features that are typical of what we have observed previously for MCO coatings [23]. Fluctuations in the Mn and Co profiles are consistent with
this region being a mixture of the tetragonal Mn$_2$CoO$_4$ and cubic MnCo$_2$O$_4$ phases, which co-exist for Mn$_{1.5}$Co$_{1.5}$O$_4$ at room temperature [28]. The distribution of the phases in this sample is revealed more clearly in axial BF TEM images such as Figure 6.8. Diffraction patterns obtained from the Cr$_2$O$_3$ and RL layers (not shown) were consistent with the rhombohedral corundum and cubic spinel structures, respectively.

6.2.3 Microstructure and Chemistry of Spinel RL after 1000 Hr. Exposure

To investigate the microstructural evolution in MCO-coated H230, a coated coupon oxidized for 1000 h at 800 °C was FIB-sectioned for TEM analysis. Figure 6.9 is a selection of images from an STEM EDXS mapping experiment comprising a DF STEM image and chemical maps of Cr, Mn, Co, W, Ni, O and Al. Each map represents a grid of 256 x 200 measurements taken using a 100 eV window centered around the K-peak for each element. The data was acquired by scanning over the same region 2048 times with a dwell time at each point of 0.2 ms for a total acquisition time of around 5.8 h. The orientation of the sample is the same as that shown in Figures 6.3, 6.4, 6.7 and 6.8 (i.e. alloy on the left, coating on the right). The Cr and O maps show a bright region around 800 nm thick, consistent with what we would expect for a Cr$_2$O$_3$ layer. To the right of this layer is a diffuse region 1-1.2 μm thick that contains Co, Cr, Mn and O, as one might expect for the RL. On the right is a region containing Co, Mn and O, with Co-rich and Mn-rich patches consistent with the MnCo$_2$O$_4$ and Mn$_2$CoO$_4$ phases of Mn$_{1.5}$Co$_{1.5}$O$_4$. The Al and O maps also show a band of internal oxides 150-200 nm in diameter beneath the Cr$_2$O$_3$ scale.

An EDXS compositional profile obtained from this sample is shown in Figure 6.10. Here again, Figure 6.10(a) is a bright field STEM image and Figure 6.10(b) is the profile obtained using EDXS along the line indicated in (a). On the left is a 1 μm region corresponding to the
alloy with depletion of Ni and Cr at the surface and enrichment in W as compared to the base alloy composition. The next 800 nm is the chromia scale. The 1.2 μm thick region adjacent to the chromia scale is the RL within which the Cr content decreases from 30 wt.% at the chromia interface to less than 5 wt.% Cr at x = 3 μm. In contrast, the Mn content increases from 8 to 25 wt.% and the Co content increases from 20 to 30 wt.% over the same distance. The region on the right shows fluctuations in Mn and Co content consistent with this being the MCO coating.

An axial BF TEM image from this sample is shown in Figure 6.11(a). The darker region on the left is the alloy substrate. Adjacent to this is a polycrystalline region which varies in thickness between 0.75 and 1.0 μm. A SADP obtained from the point marked “1” in this region is shown in Figure 6.11(b), and the spacings in this pattern are consistent with this being polycrystalline Cr₂O₃ with the corundum structure as expected. The next layer is the RL, which ranges in thickness from 0.6 to 1.2 μm. A SADP obtained from the point marked “2” in this region is given in Figure 6.11(c), and this corresponds to the [111] pattern from a cubic spinel with a₀ = 0.82 nm. This region can be readily distinguished from the MCO coating on the right because the latter region exhibits a fine twinned or faulted structure. Figure 6.11(d) is a SADP obtained from the point marked “3” in the coating and this has measured d-spacings that match that of the MnCo₂O₄ cubic phase (a₀ = 8.28 Å).

6.3 Discussion

In the following sections, we firstly compare the oxidation behavior observed in our study for bare H230 with what has been reported previously in the literature. We then consider the ways in which the coating microstructure develops through the reduction and re-oxidation processes and during subsequent extended exposure. Next, the character of the RL formed is
compared with that observed in our previous studies on MCO-coated Crofer 22APU. Lastly, the implications of these observations for SOFC performance are discussed.

6.3.1 Oxidation of Bare H230

In this study we obtained a value of $k_g = 8.8 \times 10^{-9} \text{ mg}^2 \text{cm}^{-4} \text{s}^{-1}$ for bare H230. This is similar to the parabolic oxidation rate constant values reported previously for this alloy at 800°C in air. England and Virkar reported a value of $k_g = 4.64 \times 10^{-12} \text{ g}^2 \text{cm}^{-4} \text{h}^{-1}$ ($1.29 \times 10^{-9} \text{ mg}^2 \text{cm}^{-4} \text{s}^{-1}$) for bare H230 oxidized for up to 10,000 h, but they noted that the (weight gain/area)$^2$ vs. time plots were non-linear for short exposure times [52]. Fontana et al. considered exposure times of up to 100 h and reported a value of $k_g = 2.8 \times 10^{-15} \text{ g}^2 \text{cm}^{-4} \text{s}^{-1}$ ($2.8 \times 10^{-9} \text{ mg}^2 \text{cm}^{-4} \text{s}^{-1}$); they noted that while the overall form of the weight gain curve was parabolic, the curve was very “wavy” [36]. In previous work by the current authors, a value of $k_g = 2.61 \times 10^{-8} \text{ mg}^2 \text{cm}^{-4} \text{s}^{-1}$ was obtained for bare H230 exposed to the coating reduction treatment (4 h at 850 °C under flowing Ar/3%H$_2$O/2.75%H$_2$) prior to oxidation in air at 800 °C [48]. Jian et al. studied the oxidation of bare H230 in air at temperatures of 650, 750 and 850 °C [89]. They reported multi-stage oxidation kinetics with an increase in the slope of the (weight gain/area)$^2$ vs. time plots after approximately 200 h exposure at each temperature. In the current study we did not observe a change in the oxidation kinetics, however we note that the extremely small weight gains for short-term exposures lead to greater uncertainties in these measurements that might mask such effects.

Previous studies on H230 oxidized in air at 800-900 °C have reported a two-layer oxide scale consisting of an inner Cr$_2$O$_3$ layer with an outer (Mn,Cr)$_3$O$_4$ spinel scale [9,36,52,72,92], and XRD data indicated that chromia was present as the majority phase [14, 52]. While there is a broad consensus that the outer layer of the oxide scale that forms on H230 is a spinel, there is some disagreement about the chemistry of this phase. Most authors have reported the spinel to
be either MnCr$_2$O$_4$ [72,92.] Mn$_{1.5}$Cr$_{1.5}$O$_4$ [52] or simply (M)$_3$O$_4$, where M is some unspecified transition metal [14]. Interestingly, Fontana et al. reported an outer scale of NiCr$_3$O$_4$ after 100 hrs. of oxidation at 800 °C [36]. We note that most of these previous studies have used XRD alone or a combination of XRD and SEM/EDXS to identify the crystal structure and chemistry of the phases in the scale. The unambiguous identification of spinel phases by such approaches is extremely difficult. Firstly, many of the chromite spinels have very similar lattice parameters; for example, Lu et. al showed a difference of less than 0.3% between the lattice parameters of MnCr$_2$O$_4$ and Mn$_{1.7}$Cr$_{1.3}$O$_4$ [79]. Secondly, the layers in the scales are typically thinner than the EDXS excitation volumes in SEM and thus the spectra will often include contributions from the chromia layer or even the underlying alloy substrate. These latter issues are avoided by the use of EDXS in the TEM on FIB-cut cross-sections. The TEM EDXS results reported here for bare H230 oxidized at 800°C for 1000 h show a cation ratio in the spinel that corresponds to stoichiometric MnCr$_2$O$_4$, and the SADPs obtained from these regions are consistent with the cubic MnCr$_2$O$_4$ spinel ($a_0 = 0.844$ nm).

The mechanism by which this two-layer scale forms has not been established unequivocally but can be inferred from what is known of the thermodynamics and kinetics for this system. In an analysis by England and Virkar it was shown that the oxygen partial pressure at which Mn is in equilibrium with MnO is $10^{-30}$ atm, while that for Cr/Cr$_2$O$_3$ is $10^{-28}$ atm [52]. While this implies that the thermodynamic driving force for the oxidation of Mn is somewhat higher than that for Cr, the alloy contains 0.5 wt.% Mn and 22 wt.% Cr and so one would anticipate that a chromia layer would form in the initial stages of oxidation. Since the alloy exhibits parabolic oxidation, the subsequent scale development must be dictated by mass transport through this layer. Lobnig et al. showed that the diffusion of Mn through Cr$_2$O$_3$ is up to
two orders faster than the transport of Cr [69], although subsequent studies by Sabioni et al. suggest that the difference is much smaller [70]. Thus, the scale could develop in the manner described by Saeki et al. [66,67] for oxidation of the ferritic stainless steel SS 430, which has similar Cr and Mn contents to H230 and also forms a two-layer Cr$_2$O$_3$ + MnCr$_2$O$_4$ scale. Saeki used a combination of X-ray photoelectron spectrometry and XRD to characterize the oxides formed on SS 430 in O$_2$/N$_2$ atmospheres at 1000 °C [67]. During the first 15-30 s of oxidation, a single-phase oxide layer with the corundum structure was present. Initially this layer had a chemical composition close to Fe$_2$O$_3$, but this changed rapidly to Cr$_2$O$_3$. After 30 s of oxidation an MnCr$_2$O$_4$ spinel phase was detected, which corresponded to a change in the oxidation state of Mn from +3 (Mn$_2$O$_3$) to +2 (MnCr$_2$O$_4$). It was proposed that the induction time for the formation of MnCr$_2$O$_4$ was related to the time it took to reach the maximum solubility of Mn$_2$O$_3$ in Cr$_2$O$_3$ (12-17 wt.%). Once this value was exceeded, the MnCr$_2$O$_4$ spinel nucleated on the surface and grew via a two step process involving reduction of Mn$_2$O$_3$ to MnO and a subsequent reaction between MnO and Cr$_2$O$_3$ [66,67]. Clearly, the rate of this reaction would be dictated by the transport of Mn through the Cr$_2$O$_3$ layer.

6.3.2 Development of MCO Coating Microstructure

The reactive sintering process developed by Yang et al. promotes densification of MCO by firstly reducing the dried slurry coating to a mixture of metallic Co and manganous oxide (MnO) and then re-oxidizing to (Mn,Co)$_3$O$_4$ [25]. The SEM EDXS maps shown in Figure 6.5 reveal the elemental distribution in the reduced coating. The complementary contrast in the Co and the Mn/O maps is consistent with the phase separation described by Yang et al. for this stage of the process [25]. There is also evidence of a very thin oxide layer between the H230 substrate and the coating, which indicates that a chromia layer or RL begins to form even during the reduction
treatment. It was not possible to verify the character of this layer by TEM analysis because the extensive porosity thwarted attempts to produce cross-sections by FIB. The high level of porosity revealed in Figure 6.6(a) arises because of the volumetric contraction that occurs during the reduction process. This can be estimated by considering the simplified reduction reaction:

$$\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4 (s) + 2.5 \text{H}_2 (g) \rightarrow 1.5 \text{Co} (s) + 1.5 \text{MnO} (s) + 2.5 \text{H}_2\text{O} (g)$$

For this case, the reduction of 100g of MCO would yield 37.7g of Co and 45.3g of MnO with the loss of 17g of oxygen in the form of water vapour. Taking calculated theoretical densities from known atomic weights and lattice parameters yields density values for MCO, metallic Co and MnO of 5.5, 8.8 and 5.3 g/cm$^3$, respectively this process would result in a 30% reduction in the volume of the solid.

The reduced and re-oxidized (as coated) H230 sample shown in Figure 6.6(b) exhibits a much denser coating, as expected. The STEM and TEM data shown in Figures 6.7 and 6.8, respectively reveal that there is a well-developed 200 nm thick chromia scale and a 350 nm thick (Mn,Cr,Co)$_3$O$_4$ RL. This RL comprises a cubic spinel with a Cr concentration that varies from 35 wt.% at the interface with the chromia scale to around 5 wt.% near the MCO coating. This observation is consistent with previous studies by Wang et al. on Cr$_2$O$_3$/MCO diffusion couples [78]. They showed that a two-layer RL forms with a Co-rich (Mn,Co)Cr$_2$O$_4$ spinel phase in contact with the chromia, and it was proposed that this layer may form due to the tendencies for Co$^{2+}$ and Cr$^{3+}$ ions to occupy the tetrahedral and octahedral sites in the spinel structure, respectively. The profile in Figure 6.7 also reveals small amounts of Ni and W in the RL; for example, in the region adjacent to the chromia scale the RL contains 1.2 wt.% Ni and 3.2 wt.% W. Jian et al. have also shown metallic, Ni-rich features forming on H230 heat treated in moist
hydrogen, and they attributed these nodules to volume expansion due to oxidation of Cr, which results in rejection of Ni [94].

The STEM and TEM data obtained from the sample oxidized for 1000 h at 800 °C (Figures 6.9-6.11) reveal a thickening of both the Cr$_2$O$_3$ layer and the spinel RL. The chromia layer was up to 800 nm in thickness; since there was a 200 nm thick layer in the as-coated condition, this seems to imply a modest growth rate under these conditions. It is important to note, however, that this is similar to the thickness of the chromia on the bare H230 oxidized under the same conditions (700 nm) and that the chromia is also being consumed as the RL grows. This is consistent with the conclusion of our previous studies [48] that MCO coating does not retard the kinetics of oxidation for H230 significantly. After 1000 h exposure the RL was three times thicker and exhibited a more uniform composition than that in the as-coated sample. The composition of the RL immediately adjacent to the chromia yields a spinel chemistry of Co$_{0.96}$Ni$_{0.04}$Mn$_{0.4}$Cr$_{1.6}$O$_4$. Interestingly, this corresponds exactly to (Co,Ni)(Mn,Cr)$_2$O$_4$, which may indicate that Co$^{2+}$ and Ni$^{2+}$ occupy the tetrahedral A sites while Mn$^{3+}$ and Cr$^{3+}$ occupy the octahedral B sites of the AB$_2$O$_3$ spinel structure. We also note that Cr appears to stabilize the cubic spinel crystal structure. It can be inferred from the EDXS compositional profiles in Figures 6.7 and 6.10 that approximately 5 wt% of Cr is required to stabilize the cubic structure. Once the Cr content falls below this value, oscillations in the Mn and Co profiles corresponding to MnCo$_2$O$_4$ and Mn$_2$CoO$_4$ are once again observed.

### 6.3.3 Comparison with MCO-Coated Crofer 22 APU and Implications for Performance

In a previous paper we reported a detailed TEM study of the microstructural development in MCO-coated Crofer 22 APU [59]. It was shown that a 1 µm chromia layer formed after 500 h at 800 °C in air, but there was no further thickening for longer exposures. It was inferred from
this that the system had reached a steady state in which the rate of Cr$_2$O$_3$ consumption from inward diffusion of Mn and Co to form the spinel RL was approximately equal to the rate at which the Cr$_2$O$_3$ growth front advanced into the alloy. The observations presented here seem to indicate that MCO-coated H230 does not reach this steady state condition even after 1000 h at 800 °C. The RL chemistries measured for MCO-coated Crofer 22 APU showed a maximum solubility of Cr in the spinel of approximately 35 wt.% [59]. Although the MCO-coated H230 has not reached steady state after 1000 h at 800 °C, the RL region immediately adjacent to the Cr$_2$O$_3$ layer should approximate to the steady state composition. Our EDXS data show a composition of Co$_{0.96}$Ni$_{0.04}$Mn$_{0.4}$Cr$_{1.6}$O$_4$ in this region as compared to Co$_{0.71}$Fe$_{0.06}$Mn$_{0.71}$Cr$_{1.52}$ for the RL in MCO-coated Crofer 22 APU after 1000 h at 800 °C [59]. While the Cr contents in the two RLs are nearly identical, the RL formed on the Crofer clearly has a substantially higher Mn content. This difference in Mn content in the RL may be due to differences in the rates of Mn diffusion from the alloy substrate. While the Mn contents in the two alloys are similar, the relative proportions of MnCr$_2$O$_4$ and Cr$_2$O$_3$ in the scales that form on bare H230 and Crofer 22 APU are rather different. We reported previously that MnCr$_2$O$_4$ constitutes 63-79 vol% of the oxide scale on bare Crofer 22 APU and is dependent on alloy heat treatment prior to oxidation [96]. The data obtained from H230 in the present study demonstrate clearly that MnCr$_2$O$_4$ is the minority phase in the oxide scale, although we note that the oxide scales in this case were too thin for accurate XRD quantification. This difference presumably corresponds to a more rapid egress of Mn through the Cr$_2$O$_3$ layer on Crofer 22 APU than on H230, although the reasons for this difference are not obvious.

In a previous paper we proposed a 3-layer (Cr$_2$O$_3$/RL/MCO coating) equivalent circuits model to describe the impact of RL formation on long-term SOFC performance [48]. It was
shown that the thick RLs that form on MCO-coated Crofer 22 APU result in a 5.5x lower oxidation rate than for bare Crofer 22 APU. However, MCO-coated H230 samples oxidized in air at 800 °C for 1000 h did not exhibit a lower oxidation rate than bare H230. It is conceivable that the formation of steady state RLs is required for the inhibition of oxidation kinetics and thus that these effects might only be observed for Ni-based alloys such as H230 after much longer exposures. We note that for these RLs to have a beneficial effect upon SOFC performance the spinel must have a higher electrical conductivity than the native Cr$_2$O$_3$ scale. Previous studies by Wang et al. showed that the Cr content in the (Co,Mn,Cr)$_3$O$_4$ spinel had a major influence on the overall conductivity [78]. For example, they reported electrical conductivity values of 22.2, 2.3 and 0.009 S/cm at 800 °C for Mn$_{1.25}$Co$_{1.25}$Cr$_{0.5}$O$_4$, MnCoCrO$_4$ and Mn$_{0.4}$Co$_{0.6}$Cr$_2$O$_4$, respectively. For comparison, they noted that the conductivity of Cr$_2$O$_3$ at this temperature varies between 0.006 and 0.16 S/cm, depending upon the defect content. The dramatic drop in conductivity for (Co,Mn,Cr)$_3$O$_4$ spinels with increasing Cr content is presumably due to suppression of charge transfer via polaron hopping on the Mn cations, which can occupy both octahedral and tetrahedral sites in the spinel. Since Cr$^{3+}$ has a strong preference for the octahedral sites, a high Cr content in the spinel (as in Mn$_{0.4}$Co$_{0.6}$Cr$_2$O$_4$) could lead to Mn occupying tetrahedral sites only (presumably as Mn$^{2+}$) with a corresponding dramatic reduction in the electrical conductivity. We have shown previously that the RL can dominate the oxidation kinetics once it becomes significantly thicker than the Cr$_2$O$_3$ layer in the scale [48]. Clearly, additional work is required to understand the effects of variations in the alloy and/or coating chemistry on RL formation. If, however, one could design a combination of alloy and coating for which a steady-state spinel RL would be established at an early stage, and at a low enough Cr content to prevent occupation of the octahedral sites in the spinel, then this could constitute the basis for the next
generation of coated metallic SOFC interconnects that will allow enhanced SOFC performance over long-term service.
Figure 6.1: Plot of parabolic weight gain (mg$^2$cm$^{-4}$) vs. exposure time for bare H230 exposed in static air at 800 °C. The gravimetric rate constant ($k_g$) measured from the slope of the curve was $8.8 \times 10^{-9}$ mg$^2$cm$^{-4}$s$^{-1}$. 
Figure 6.2: Plan view SEM images obtained from the surface of the scale formed on bare H230 after 1000 h oxidation in static air at 800 °C: (a) BSE image obtained with the electron beam oriented perpendicular to the scale surface; and (b) SE image obtained with the sample tilted at 52° with respect to the beam.
Figure 6.3: STEM data acquired from a FIB-cut cross-section through the alloy/scale interface of a bare H230 sample oxidized for 1000 h at 800° C: (a) BF image; (b) compositional profile obtained from spectra acquired at points along the horizontal line in (a).
Figure 6.4: TEM data acquired from a FIB-cut cross section through the alloy/scale interface of a bare H230 sample oxidized for 1000 h at 800° C: (a) BF TEM image; (b) and (c) SADPs from regions 1 and 2 in (a), respectively. The spotty ring pattern in (b) is consistent with the corundum structure of Cr₂O₃ whereas the single crystal zone axis pattern in (c) corresponds to a cubic spinel phase.
Figure 6.5: SEM data obtained from a metallographic cross-section through the MCO-coated H230 sample after the reduction step of the reactive sintering process. The BSE image shows the region analyzed and the X-ray maps show the normalized relative intensities for the Co, Mn, Cr and Ni K\(^{\text{III}}\), the W L\(^{\text{III}}\) and the O K peaks after deconvolution for peak overlap.

Figure 6.6: BSE SEM images obtained from metallographic cross-sections through MCO-coated H230: (a) after the reduction process and (b) after reduction and re-oxidation processes.
Figure 6.7: STEM data acquired from a FIB-cut cross-section through the alloy/scale interface of an as-coated MCO/H230 sample (i.e. reduced and re-oxidized): (a) BF image; (b) compositional profile obtained from spectra acquired at points along the horizontal line in (a).
Figure 6.8: BF TEM image acquired from a FIB-cut cross-section through the alloy/scale interface of an as-coated MCO/H230 sample.
Figure 6.9: STEM data acquired from a FIB-cut cross-section through the alloy/scale interface of an MCO-coated H230 sample oxidized for 1000 h at 800 °C. The DF STEM image shows the region analyzed and the X-ray maps show the normalized relative intensities for the Cr, Mn, Co and Ni K\(\text{II}\), the W L\(\text{II}\) and the O and Al K peaks.
Figure 6.10: STEM data acquired from a FIB-cut cross section through the alloy/scale interface of an MCO-coated H230 sample oxidized for 1000 h at 800 °C: (a) BF image; (b) compositional profile obtained from spectra acquired at points along the horizontal line in (a).
Figure 6.11: TEM data acquired from a FIB-cut cross section through the alloy/scale interface of an MCO-coated H230 sample oxidized for 1000 h at 800 °C: (a) BF image; (b), (c) and (d) SADPs from regions 1, 2 and 3 in (a), respectively.
Table 6.1: Composition of Haynes 230

<table>
<thead>
<tr>
<th>Ni</th>
<th>Co</th>
<th>Cr</th>
<th>Mo</th>
<th>W</th>
<th>Fe</th>
<th>Si</th>
<th>Mn</th>
<th>C</th>
<th>Al</th>
<th>B</th>
<th>La</th>
</tr>
</thead>
<tbody>
<tr>
<td>57</td>
<td>5*</td>
<td>22</td>
<td>2</td>
<td>14</td>
<td>3*</td>
<td>0.4</td>
<td>0.5</td>
<td>0.1</td>
<td>0.3</td>
<td>0.015*</td>
<td>0.02</td>
</tr>
</tbody>
</table>
Chapter 7: Conclusions and Recommendations for Future Work

7.1 Pre-Heat Treatment Effects on Crofer Oxidation

A study was performed on the effect of 1 and 4 h pre-oxidation heat treatments at 1050 °C in Ar on the oxidation kinetics and oxide scale microstructure for Crofer 22 APU oxidized in air at 800 °C for up to 750 h. The key findings of this study were:

1. The parabolic oxidation rate constant, \( k_g \), fell from \( 4.82 \times 10^{-8} \text{ mg}^2 \text{cm}^{-4} \text{s}^{-1} \) for the AR samples to \( 2.82 \times 10^{-8} \) and \( 1.41 \times 10^{-8} \text{ mg}^2 \text{cm}^{-4} \text{s}^{-1} \) for the HT1h and HT4h samples, respectively.

2. All of the oxidized samples exhibited: a two-layer oxide scale with a continuous inner \( \text{Cr}_2\text{O}_3 \) layer and a discontinuous outer \( \text{MnCr}_2\text{O}_4 \) spinel layer, subscale \( \text{MnCr}_2\text{O}_4 \) spinel pockets protruding into the alloy, and internal Ti-rich oxide precipitates with the monoclinic TiO\(_x\) structure.

3. Both the grain size of the outer \( \text{MnCr}_2\text{O}_4 \) spinel layer and the proportion of this phase in the oxide scale increased with alloy pre-heat treatment and increasing alloy grain size.

4. The scale microstructures for samples oxidized for just 5 h indicate that the nucleation of the \( \text{Cr}_2\text{O}_3 \) and \( \text{MnCr}_2\text{O}_4 \) phases during the initial stages of oxidation influences the final scale microstructures. Larger alloy grain sizes lead to lower nucleation rates, larger spinel grains, and improved oxidation resistance.

It is inferred from these observations that: the larger alloy grain sizes in the heat-treated samples reduce the initial supply of Mn to the alloy surface; this leaves more Cr available to form a thicker initial \( \text{Cr}_2\text{O}_3 \) scale with coarser grains; and the effect of this layer on the transport of Mn and Cr is what leads to the reduction in \( k_g \). Thus, alloy heat-treatment is an effective way of slowing the oxidation of Crofer 22APU. It is suggested that a combination of alloy heat-
treatment and MCO coating could result in better oxidation resistance and inhibition of chromia volatility in SOFC interconnect applications than coating alone.

7.2 RL’s on MCO Coated Crofer Conclusions

Coatings of MCO have been deposited on Crofer22 APU substrates by a slurry process followed by reduction and re-oxidation to promote sintering. Microstructural analysis by TEM and EDXS techniques on FIB-cut cross-sections through as-coated samples and samples after oxidation at 800°C in air for 250 and 1000 h have revealed the following features:

1. The as-coated samples have a thin (0.7 mm) chromia scale at the alloy/coating interface and a thicker (>3 mm) RL comprising a Co/Cr-rich spinel between the chromia and the MCO. The interface between the RL and the MCO is rather rough and with regions of this spinel penetrating between the MCO grains in the layer above.

2. The 250 h samples have a slightly thicker (1.0 mm) chromia scale but a significantly thinner (1.5e2.0 mm) and more well defined spinel RL. This spinel contains significantly more Mn and Co but less Cr than that in the as-coated sample. There are also internal Ti-rich oxides in the Crofer22 APU below the chromia scale and stoichiometric SS pockets of the cubic spinel MnCr2O4 at the chromia/alloy interface.

3. The 1000 h samples show very little thickening of the chromia scale, or further development of the SS pockets and internal oxides. The spinel RL is, however, much thicker (>4 mm) with a uniform composition of around Mn1.38Co0.84Cr0.54Fe0.24O4.

We infer that these unusual changes in the thickness, morphology and composition of the
spinel RL are related to changes in the diffusive fluxes during the development of the coating microstructure. Thus, the observations can be rationalized if there is: segregation of metallic Co to the coating/substrate interface with outward diffusion of Cr from the alloy in the reduction stage; conversion of the metallic layer to Co/Cr-rich spinel during subsequent re-oxidation; reversion of the Co/Cr-rich spinel to more MCO-like phases during the earlier stages of exposure; and development of Cr-doped MCO-like phases in the RL during subsequent evolution of the chromia layer as oxidation proceeds. These observations could have important consequences for the understanding of degradation mechanisms in SOFC interconnects produced from MCO-coated Crofer22 APU since we anticipate that both the RL spinel and the SS MnCr2O4 pockets will have lower electrical conductivities than the MCO.

7.3 Haynes 230 Oxidation and RL Formation Conclusions

A combination of thermogravimetric analysis and electron microscopy techniques has been used to study the development of oxide scale and coating microstructures for bare and MCO-coated H230. The main findings of this study are:

1. A parabolic rate constant of $8.8 \times 10^{-9}$ mg$^2$cm$^{-4}$s$^{-1}$ was measured for the oxidation of bare H230 at 800 °C for up to 1000 h. The scale consisted of a 700 nm thick continuous Cr$_2$O$_3$ layer with a discontinuous 300 nm tabular MnCr$_2$O$_4$ spinel overlayer.

2. For MCO-coated H230 the reduction step of the reactive sintering process results in a mixture of metallic Co and MnO phases. The reduced coating is highly porous due to the large (~30%) volume contraction upon reduction. A thin Cr-rich oxide scale forms at the alloy/coating interface during the reduction process.
3. Following the re-oxidation step of the reactive sintering process, the coating is much denser and the interfacial microstructure consists of a 200 nm thick Cr$_2$O$_3$ scale and a 400 nm thick cubic spinel RL. The measured chemistry of the spinel RL adjacent to the Cr$_2$O$_3$ layer was (Co$_{0.87}$Ni$_{0.06}$W$_{0.05}$Mn$_{0.16}$Cr$_{1.86}$)O$_4$.

4. Oxidation of MCO-coated H230 at 800 °C for 1000 h resulted in a thickening of the Cr$_2$O$_3$ layer to 800 nm and the cubic spinel RL to ≈ 1.2 μm. In this case the chemistry measured adjacent to the Cr$_2$O$_3$ layer was (Co$_{0.96}$Ni$_{0.04}$Mn$_{0.4}$Cr$_{1.6}$)O$_4$.

It was noted that these RLs are substantially thinner than those observed in our previous study on for MCO-coated Crofer 22 APU oxidized under the same conditions [23]. Since the MnCr$_2$O$_4$ spinel overlayer formed during oxidation of bare H230 is also significantly thinner than that for bare Crofer 22 APU [24], it is proposed that differences between the diffusive fluxes of Mn and Cr can a dramatic effect on RL formation rate.

### 7.4 Recommended Future Work

While the work presented in this thesis is the first known published data on reaction layers which form on ferritic and Ni-base superalloys coated with MCO, there is clearly much more work to be done. Using slurry based coatings for this study has proven very difficult as the coatings tend to be very porous and have inconsistent thicknesses and densities. The following is recommended future work/experiments, some of which are already in progress:

1) RLs which form on MCO coated Haynes 230 have formation kinetics that are quite sluggish. Additional experiments on this alloy/coating system need to be run either at much longer times (5,000-10,000 hrs) or at elevated temperatures (>800 °C) in order to
better understand this RL, how it forms and what the equilibrium composition of the RL is.

2) While some electrical conductivity exists on spinel materials that are close in chemistry to the RLs that form on Crofer 22 APU and H230, there have been no published studies on conductivities of real RLs. This may be done by synthesizing chemistries similar in composition to the RL and performing bulk 4-point electrical conductivity measurements.

3) Understanding diffusive fluxes and rates of RL formation are critical to predicting long-term performance properties for SOFCs. In order to do this, model coating systems must be used on substrates of interest. These model coating systems would likely be deposited via PLD and would be thin, dense and homogeneous in nature.

4) In order to understand how RLs form under real SOFC operating conditions, it is necessary to examine RLs which form during area specific resistance (ASR) testing. The applied electrical current in these tests will enable understanding of how RLs form under actual operating conditions.

5) Additional accelerated testing is needed in order to better predict long-term properties. This may be done on model coating systems by exposing the same samples to temperatures above the actual use temperature (800 °C) and correlating RL chemistry and thickness to determine how one might develop an accelerated test.
References


[2]. www.seca.doe.gov


