OXIDATION KINETICS OF METALLIC INTERCONNECTS FOR INTERMEDIATE TEMPERATURE SOFC

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ABSTRACT

The oxidation kinetics of metallic interconnects with protective oxide coatings, for use in planar SOFC stacks, was investigated. An oxidation kinetics model was developed for coated interconnects based on the chemical diffusivities of the participating species. The model indicates that there are two limiting cases of oxidation kinetics for a coated metallic interconnect, 1) linear with time, where oxidation is limited by the coating, and 2) parabolic with time, where the coating is ineffective in suppressing oxidation kinetics. The oxidation behavior of a Ni-Cr alloy coated with two different protective oxide layers, the perovskite phase La$_{0.85}$Sr$_{0.15}$MnO$_3$ and the spinel phase Mn$_2$CrO$_4$, was studied in air at 800°C. After oxidation for extended periods of time, it was observed that a scale of oxide, comprised primarily of Cr$_2$O$_3$ and a trace amount of the spinel phase Mn$_{2.4}$Cr$_{0.6}$O$_4$, formed under the protective coating. The oxidation kinetics of the oxide coated metallic interconnects were shown experimentally to exhibit linear behavior with time indicating that the coatings were effective in reducing the oxidation kinetics.

INTRODUCTION

In intermediate temperature solid oxide fuel cell (IT-SOFC) planar stacks, it is desirable to use metallic interconnects due to potential low cost and flexibility in fabrication. However, it is well known that the oxidation of metallic interconnects at SOFC operating temperatures (700-800°C) is responsible for the majority of the degradation in stack performance with time and ultimately limits the design life of the stack. The majority of the alloys used to date for metallic interconnects are either stainless steels or nickel-chromium-based superalloys. These alloys readily oxidize in both oxidant and fuel environments at the SOFC operating temperatures of 700 to 800 °C, forming an oxide scale that primarily consists of chromium oxide, Cr$_2$O$_3$ (1,2). Although Cr$_2$O$_3$ is an electronic conductor, its conductivity is low (~10$^{-5}$ S/cm at 800 °C) and thus the growth of this oxide scale significantly increases the resistance of the interconnect and the stack with time (3,4). In addition, chromium tends to evaporate from the oxide layer, which
can lead to loss of physical contact with the cell and/or poisoning of the cathode (5,6). Thus, as-received, commercially available chromium containing alloys are not suitable for application as interconnects.

One approach to reducing the oxidation kinetics of the alloy and suppress the loss of chromium through the vapor phase is the use of protective coatings (7). A protective coating is a dense layer, most often an oxide, that is deposited directly on the metallic interconnect. Suitable coating materials should meet the following criteria: 1) slow ion transport to reduce oxidation kinetics, 2) high electronic conductivity, and 3) stable at SOFC operating temperatures and atmospheres. Two classes of materials that are thermodynamically stable, bond well to metals, and exhibit acceptable conductivity are the spinel and perovskite phases containing transition elements. For example, Cr-based oxide spinels have conductivities that are orders of magnitude higher than Cr$_2$O$_3$, $10^{-4}$ to $3$ S/cm$^2$ at $800^\circ$C, and exhibit limited anion transport. Even more promising is the perovskite phase Sr-doped LaMnO$_3$, which is primarily an electronic conductor with a conductivity of 200 to 500 S/cm at $800^\circ$C. The Mn-based perovskites exhibit low oxide ion transport, which is necessary for oxidation protection (8,9). Although other perovskite phases, including the Sr-doped LaCoO$_3$ and LaFeO$_3$ systems, exhibit higher electronic conductivity (400 to 1000 S/cm at $800^\circ$C), their high oxide ion conductivity precludes their use as a protective coating (10,11).

The high temperature oxidation kinetics of uncoated alloys typically exhibits parabolic growth rates with time and conforms to the Wagner model. The objective of using a protective oxide coating is to suppress the oxidation rate of the metal to some value below the parabolic rate. The effectiveness of the coating in reducing oxidation rates and the behavior of the oxide formation is largely a function of the transport properties of the coating material and its thickness. For example, a number of oxide formation scenarios exist for chromium-containing alloys coated with a protective coating which is predominantly electronic conductor. If the ionic conductivity of the protective coating is primarily oxide ion conductivity and the ionic conductivity of the native oxide scale is primarily cation conductivity (with still the total conductivity dominated by electronic conductivity), the oxide will grow under the productive coating at the coating/native oxide interface. Similarly, if the ionic conductivity of both the protective and native oxide layers is primarily oxide ion conductivity, the oxide will grow under the coating but at the alloy/native oxide interface. However, if the ionic conductivity of both the protective and native oxide layers is primarily cation conductivity, the possibility exists that the newly formed oxide scale will grow on top of the protective coating. These three simple examples are only a few of the possible cases and serve to highlight the importance of understanding the underlying transport mechanisms through the coatings and the oxide scale, and subsequent interactions with the alloys. The objective of this work was to develop an understanding of the oxidation behavior of alloys with protective coatings, and develop a model that would guide the selection and development of potential coating materials for use with SOFC metallic interconnects. All of the work was conducted on one of the commercially available Ni-Cr alloys. However, the general principles and approach should be applicable to other Ni-Cr alloys as well as stainless steels containing Cr.
THEORETICAL ANALYSIS

The kinetics, location, and type of oxide layer that develops during high temperature oxidation of a coated metallic interconnect depend largely on the type of ion diffusivity in both the coating and in the native oxide scale. As described previously, the oxide scale formed during oxidation can grow either under or over the deposited coating layer depending on the transport properties of the two layers. For the case of oxide formation under a protective coating, a simple theoretical analysis of oxidation kinetics is presented.

The oxidation kinetics of an oxide layer forming under a protective coating can be modeled in terms of the chemical diffusivities of the participating species as shown in the schematic in Figure 1. In this case, it is assumed that the oxide ion diffusivity is higher than the cation diffusivity in the coating layer, and that the cation diffusivity is higher than the oxide ion diffusivity in the formed oxide scale (which is predominantly Cr₂O₃). In such a case, the oxide scale forms under the protective coating and growth initiates from the coating/Cr₂O₃ interface. The electronic transport is assumed to be faster than the ion transport, in both layers, and thus not a limiting factor. The metallic interconnect alloy investigated in this work was Haynes 230, a Ni-Cr superalloy from Haynes International, whose native oxide primarily consists of Cr₂O₃ with small traces of the spinel phase (Mn₃Cr₁)O₄. The analysis, however, should be applicable to any chromia forming alloy. The thickness of the as-deposited coating is given by \( X_c \), and the thickness of the Cr₂O₃ formed under the coating as a function of time is given by \( X_d \), as shown in Figure 1. The boundary conditions are the partial pressure of oxygen at the coating-atmosphere interface, \( p_{O_2}^o \), and the activity of Cr at the alloy-chromia interface, \( a_{Cr}^o \).

![Figure 1. Schematic showing oxidation under a protective coating. The kinetics can be modeled using the chemical diffusivities and activities of the participating species.](image-url)
The growth of the Cr$_2$O$_3$ oxide layer is assumed to originate at the coating/Cr$_2$O$_3$ interface with O$^{2-}$ and Cr$^{3+}$ ions diffusing from the boundaries to this interface. The flux of oxide ions through the coating to the interface is given by,

$$J_O = -\frac{\tilde{D}_O C_O}{RT} \nabla \mu_O = \frac{\tilde{D}_O C_O}{2X_c} \left( \ln p_{O_2}^o - \ln p_{O_2}^{\text{int}} \right)$$  \[1\]

where $\mu_O$ is the chemical potential of oxygen, $\tilde{D}_O$ is the chemical diffusion coefficient of O in the coating, $C_O$ is the concentration of O in the coating, and $p_{O_2}^{\text{int}}$ is the equilibrium partial pressure of oxygen at the coating/Cr$_2$O$_3$ interface. In the preceding it is assumed that $\tilde{D}_O$ is independent of composition, and thus of position. The flux of chromium ions transported through the Cr$_2$O$_3$ oxide scale to the interface is similarly given by,

$$J_{Cr} = -\frac{\tilde{D}_{Cr} C_{Cr}}{RT} \nabla \mu_{Cr} = \frac{\tilde{D}_{Cr} C_{Cr}}{X_d} \left( \ln a_{Cr}^o - \ln a_{Cr}^{\text{int}} \right)$$  \[2\]

where $\mu_{Cr}$ is the chemical potential of chromium, $\tilde{D}_{Cr}$ is the chemical diffusion coefficient of Cr in the formed oxide scale, $C_{Cr}$ is the concentration of Cr in the oxide scale, $a_{Cr}^{\text{int}}$ is the equilibrium activity of Cr at the coating/Cr$_2$O$_3$ interface. In the preceding it is assumed that $\tilde{D}_{Cr}$ is independent of composition, and thus of position. The formation of Cr$_2$O$_3$ at the interface is given by the reaction,

$$2Cr + \frac{3}{2}O_2 \rightarrow Cr_2O_3$$  \[3\]

with the equilibrium constant given by,

$$K_{eq} = \exp \left( \frac{-\Delta G^o}{RT} \right) = \frac{a_{Cr}^{\text{int}}}{\left( a_{Cr}^o \right)^{3/2}} p_{O_2}^{\text{int}}$$  \[4\]

where $\Delta G^o$ is the standard free energy for the reaction in Equation [3], $a_{Cr}^{\text{int}}$ and $a_{Cr}^o$ are respectively the activities of Cr$_2$O$_3$ and Cr at the interface, and $p_{O_2}^{\text{int}}$ is the equilibrium partial pressure of oxygen at the interface. In what follows, it will be assumed that Cr$_2$O$_3$ is of stoichiometric composition such that $a_{Cr}^{\text{int}} = 1$. If equilibrium conditions are assumed, the formation of Cr$_2$O$_3$ establishes the partial pressure of oxygen in the oxide as a function of Cr activity. Knowing the density of Cr$_2$O$_3$ and the reaction in Equation [3], the flux of oxide and chromium ions can be directly related to the thickness of the Cr$_2$O$_3$ oxide as a function of time by,
\[
\frac{J_{Cr}}{2} = \frac{J_O}{3} = \frac{N_A}{V_C} \frac{d[X_d(t)]}{dt}
\]

where \( N_A \) is Advoagadro’s number, \( V_C \) is the molar volume of \( \text{Cr}_2\text{O}_3 \), and \( t \) is time. Solving equations [1], [2], [4], and [5] for the thickness of the oxide layer formed, \( X_d \), as a function of time gives the following expression,

\[
X^2_d + \frac{9D_{Cr}C_crX_c}{2D_OC_O} X_d = \frac{3V_CD_{Cr}C_cr}{4N_A} \left[ \frac{4}{3} \ln a_{Cr}^o - \frac{2}{3} \frac{\Delta G^o}{RT} - \ln p_{O_2}^o \right] t
\]

The growth rate of the oxide scale of thickness \( X_d \) is a function of both the diffusivity of the chromium ions in the scale, namely \( D_{Cr} \), and the diffusivity of oxide ions in coating, namely \( D_O \). Equation [6] suggests two limiting cases based on the relative magnitudes of the diffusivities of the participating species. The following describes the two limiting cases.

**Case A: Parabolic Kinetics - Diffusion Controlled:** \( X_d \gg \frac{9D_{Cr}C_crX_c}{2D_OC_O} \)

In this case, the \( D_O \) in the deposited coating is significantly greater than the \( D_{Cr} \) in the growing oxide scale and/or the oxide coating is very thin, such that the above condition is satisfied. In such a case, the oxidation kinetics is dictated by \( D_{Cr} \) in the formed \( \text{Cr}_2\text{O}_3 \) scale. In this limiting case, the oxide thickness \( X_d \), is given as a function of time by,

\[
X_d \approx \sqrt{\frac{3V_dD_{Cr}C_cr}{4N_A} \left[ \frac{4}{3} \ln a_{Cr}^o - \frac{2}{3} \frac{\Delta G^o}{RT} - \ln p_{O_2}^o \right]} t
\]

The oxidation kinetics of the growing oxide scale is parabolic with time, consistent with a diffusion-controlled process. Therefore, the coating layer is ineffective and the oxidation kinetics is governed solely by the kinetics of the native-forming oxide scale, \( \text{Cr}_2\text{O}_3 \). This is not the desired situation for a coated metallic interconnect wherein the protective coating is intended to suppress the oxidation kinetics of the base alloy.

**Case B: Linear Kinetics - Interface Controlled:** \( X_d \ll \frac{9D_{Cr}C_crX_c}{2D_OC_O} \)

In this case, the \( D_O \) in the coating is significantly lower than \( D_{Cr} \) in the oxide scale formed under the coating and/or the oxide coating is very thick, such that the above condition is satisfied. Thus, the oxidation kinetics is limited by the \( D_{Cr} \) in the coating. In this limiting case, the oxide scale thickness \( X_d \), is given as a function of time by,

\[
X_d \approx \frac{D_OC_OV_C}{6N_AX_c} \left[ \frac{4}{3} \ln a_{Cr}^o - \frac{2}{3} \frac{\Delta G^o}{RT} - \ln p_{O_2}^o \right] t
\]
The growth rate of the oxide scale thickness $X_d$ is only a function of the oxide ion diffusivity, namely $D_O$, in the coating and is independent of $D_{Cr}$ in the oxide scale. The oxidation kinetics of the growing oxide scale is linear with time, similar to an interface-controlled process. This is the desired case for metallic interconnects, where the deposited coating controls and limits the oxidation kinetics of the base alloy.

An illustrative calculation using Equation [6] demonstrating the transition region between the two limiting cases is shown in Figure 2. The oxide thickness, $X_d$, is graphed as a function of the chemical diffusion coefficient of O in the coating, $D_O$, for an alloy with an assumed chromium chemical diffusivity, $D_{Cr}$, of $10^{-15}$ cm$^2$/s in the native oxide scale. Results are presented for two different coating thicknesses, $X_c$ of 1 µm and 10 µm, after oxidation at 800 °C for 1000 hours. As shown in Figure 2, a transition region exists below which the diffusivity of the coating limits the oxide growth rate. If the $D_O$ in the coating is too high, in this case greater than $10^{-14}$ cm$^2$/s, then the coating is ineffective in suppressing the oxidation kinetics of the alloy over the regime calculated. For $D_O$ less than $10^{-14}$ cm$^2$/s, the growth rate of the oxide layer significantly decreases with decreasing oxygen chemical diffusivity. Note also that over this range, the thicker the coating, $X_c$, the smaller is the oxide scale formed, $X_d$, in a given time (1000 h in this illustration). However, above the transition, the $X_c$ has little effect over the range calculated ($X_c \leq 10$ mm).

Figure 2. Illustrative calculation of Equation [6], showing oxide layer thickness, $X_d$, as a function of $D_O$ in the coating layer.
EXPERIMENTAL

Dense protective coatings of spinel and perovskite phases were directly deposited on Haynes 230 foils by sputtering. The sputtering targets with the desired compositions and crystal structures were fabricated by conventional ceramic processing methods. The two oxides investigated were the perovskite phase La_{0.85}Sr_{0.15}MnO_3 (LSM) and the spinel phase Mn_2CrO_4. X-ray diffraction was used to confirm that the desired phases were successfully synthesized and single phase. Deposition was conducted in a Denton Vacuum LCC Discovery 18 Sputtering System with RF sputtering at a power of 200 W in an Argon atmosphere at 3.0 x 10^{-6} torr. Oxide coatings with a range of thicknesses between 0.2 and 2 µm were deposited on 5 mil thick foils of Haynes 230. The as-deposited oxide coatings were dense, yet amorphous. Therefore, after deposition the coated samples were heated at 800 °C for 2 hr in order to crystallize the oxide-coating. Sample coupons with coatings were oxidized in air at 800 °C for various periods of time. The samples were sectioned, mounted, and polished for analysis using optical and scanning electron microscopy (SEM). Before and after oxidation studies, elemental analysis of the oxide layers was conducted with energy dispersive spectroscopy (EDS). The thicknesses of the as-deposited coating and the oxide scale formed during high temperature oxidation were measured in an SEM.

RESULTS AND DISCUSSION

Sample coupons of Haynes 230 with spinel and perovskite protective oxide coatings were oxidized in air at 800 °C for various periods of time and analyzed using SEM, EDS, and XRD. An SEM micrograph (backscattered electron image) of an LSM-coated Haynes 230 sample after oxidation for 14 days at 800 °C in air is shown in Figure 3. The oxide is comprised of two distinct layers, the original deposited LSM coating of thickness \( X_d \) on the top and an oxide scale of thickness \( X_c \) that has formed under the protective LSM coating. From XRD and EDS analyses, the oxide formed under the LSM coating is primarily comprised of Cr_2O_3 with a trace amount of the spinel phase Mn_{2-x}Cr_xO_4, the native oxides that normally occur on oxidized Haynes 230. The formation of an oxide scale under the protective coating indicates that oxide ions diffused through the LSM coating and oxidized Cr and Mn from Haynes 230. This also implies that Mn and Cr from the alloy diffuse out of the alloy towards the interface, and their transport through the alloy is not rate-limiting. Similar results were obtained on Mn_2CrO_4 spinel coated samples with a two phase, Cr_2O_3 and Mn_{2-x}Cr_xO_4 (trace) oxide scale forming under the coating. These results are in agreement with the scenario depicted in the proposed kinetic model for oxidation under a protective coating.

The oxidation kinetics of LSM and Mn_2CrO_4 coated Haynes 230 samples were investigated at 800 °C in air. Initially, a dense layer of coating of thickness, \( X_c \), of 1.3 µm was deposited on Haynes 230 substrates by sputtering. During oxidation, an oxide scale of thickness \( X_d \) formed under the protective coating. The total oxide thickness, \( (X_d + X_c) \), is plotted as a function of time in Figure 4 for both types of coatings, LSM and spinel. The oxidation kinetics for samples with both coatings is linear in time.
Figure 3. Backscattered electron (BSE) image of a cross section showing the formation of a Cr$_2$O$_3$ oxide scale under the LSM coating after oxidation in air at 800°C for 14 days.

Thus, the oxidation kinetics are dictated and controlled by the protective coating as proposed in Equation 8. The rate of oxide growth under the LSM coating is $\sim 1.1 \times 10^{-6}$ μm/sec while that under the spinel coating is $\sim 3.5 \times 10^{-6}$ μm/sec. The higher growth rate under the spinel was not expected, since spinel phases are thought to be primarily cation ion conductors. However, little or no data are available about the oxide ion conductivity...
in spinels at high temperatures. Based on these growth rates, the chemical diffusivity of oxygen in the coating, namely $D_O$, can be estimated using Equation 8. The estimated $D_O$ is $\sim 6 \times 10^{-16} \text{ cm}^2/\text{s}$ in LSM and $\sim 2 \times 10^{-15} \text{ cm}^2/\text{s}$ in the spinel phase. The chemical diffusivity of Cr in the formed oxide scale, $D_{Cr}$, cannot be determined from the present data. In order to determine $D_{Cr}$, it will be necessary to conduct experiments for times long enough that the kinetics eventually switch over to diffusion control through the oxide scale formed – that is the parabolic limit. However, since the oxidation rates are linear with time, it can be surmised that the chemical diffusivity of Cr must be greater than $10^{-14} \text{ cm}^2/\text{s}$.

The effectiveness of the coatings in suppressing the oxidation kinetics can be predicted for longer times using Equation 6. For an LSM coating of 1.3 μm and a chemical diffusivity of oxide ions in LSM, $D_O$, of $6 \times 10^{-16} \text{ cm}^2/\text{s}$, the oxide thickness, $X_d$, as a function of time at 800 °C, with and without an LSM coating, was calculated for two different assumed values of Cr diffusivity, $D_{Cr}$. Figures 5 and 6 show oxide thickness, $X_d$, as a function of time for a Cr diffusivity, $D_{Cr}$, of $10^{-14}$ and $10^{-13} \text{ cm}^2/\text{s}$, respectively. The oxidation kinetics of the uncoated alloy is parabolic, as shown for both values of Cr diffusivity. However, the oxidation kinetics of the coated samples initially exhibit linear behavior at shorter periods of time. Depending on the relative values of the Cr and O diffusivities, the coated samples will ultimately exhibit parabolic growth at some point. As shown in Figure 5, the parabolic term begins to have an effect after about 300 days, whereas in Figure 6, the coated sample exhibits linear behavior for more than 1000 days. In both cases, the coating significantly decreases the oxidation kinetics of the alloy and thus reduces the total thickness of the oxide scale.

![Figure 5](image_url)

Figure 5. Calculated oxide thickness as a function of time at 800° C for an uncoated and LSM coated alloy with a Cr diffusivity of $10^{-14} \text{ cm}^2/\text{s}$ in the oxide scale.
Figure 6: Calculated oxide thickness as a function of time at 800° C for an uncoated and LSM coated alloy with a Cr diffusivity of $10^{-13}$ cm$^2$/s in the oxide scale.

CONCLUSIONS

A model for the oxidation kinetics of metallic interconnects coated with a protective oxide layer was developed. Model takes into account transport through both the oxide scale formed and the deposited coating. Depending upon the relative transport properties of the coating and the oxide scale formed, the thickness of the coating, and the time of oxidation, the oxide scale formed exhibits two limiting behaviors: (a) If transport through the coating is sluggish and the coating thickness is large, the oxide scale thickness varies linearly with time. In such a case, the coating is effective in suppressing the oxidation kinetics of the alloy. (b) If transport through coating is rapid, and if the coating thickness is small, the oxide scale thickness is proportional to the square root of time – parabolic kinetics. In such a case, the coating is ineffective in suppressing oxidation kinetics, which are governed by the transport properties of the oxide scale. Protective coatings, comprised of the perovskite phase $La_{0.85}Sr_{0.15}MnO_3$ (LSM) and the spinel phase $Mn_2CrO_4$ of thickness on the order of 1 to 2 microns, were shown to be effective in suppressing the oxidation kinetics. In both cases, the oxidation kinetics exhibited linear behavior with the oxidation time, indicating that the kinetics was dictated by transport through the coating. Also, the oxide scale formed under the coating, indicating that predominant ionic species transporting through the coating was oxygen. It was further observed that LSM was about three times more effective in suppressing oxidation kinetics as the spinel. The $D_O$ at 800 °C was estimated to be $\sim 6 \times 10^{-16}$ cm$^2$/s in LSM and $\sim 2 \times 10^{-15}$ cm$^2$/s in Mn-Cr spinel.

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