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Lifetime prediction for manganese cobalt spinel oxide coatings on metallic interconnects

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ABSTRACT

To prevent chromium poisoning of cathodes in solid oxide fuel cells, metallic interconnects are coated with protective oxides. One commonly used coating is manganese cobalt spinel oxide (MCO). Although MCO acts as a barrier to oxidation of interconnects, formation of native oxide scales on interconnects still occurs. As a result of native scale growth during fuel cell operations, the strength of the MCO interface will degrade. In addition, the spallation is generally driven by the temperature coefficient of expansion mismatch between the native scales and the MCO. Thus MCO spallation is likely to be dependent on the thicknesses of the different layers and is most likely to occur when cooling the fuel cell from high operating temperatures. In this study, the effects of the native scale thickness on MCO spallation are explored. To obtain interfacial fracture energy as a function of native scale thickness, room temperature, four-point bend experiments are performed on coated interconnects with various native scale thicknesses. By comparing the evolving interfacial fracture energy from experiments with the interfacial fracture energy obtained from an analytical model, coating lifetime is predicted.

1. Introduction

To prevent chromium (Cr) migration from chromium alloyed iron (Fe) based interconnects to cathodes, interconnects of solid oxide fuel cells (SOFCs) are coated by manganese cobalt spinel oxides (MCO) [1–5]. Although several researchers have found MCO coating to be an effective barrier to both chromium outward migration and oxygen inward diffusion, native scales (Cr_2O_3) of interconnects are formed beneath the MCO coatings by oxidation heat treatment and there is then a significant decrease in the coating adhesion [6]. It is anticipated that, in spite of interconnects being protected by MCO coatings, the native scales will still grow in thickness during stack operations and will experience growth stresses. In addition, thermal coefficient of expansion (TCE) mismatch between the native scales and MCO coatings will result in the development of thermal stresses in the coatings when experiencing temperature changes during fuel cell shut down.

There are several reasons why intrinsic stresses occur during scale growth. One important source of intrinsic or growth stresses is epitaxial constraint. Differences between lattice parameters of the oxide and substrate cause stresses to become maximum in oxide-metal phase boundaries. The stresses fall off toward the oxide surface. Borie et al. [7] employed X-ray techniques to reveal that thin oxide films on copper are strained because of the epitaxial relationship between the oxides and underlying material. Epitaxial stresses are only important for thin oxide scales as they are inversely related to the oxide scale thickness [7].

Appleby et al. [8] studied the effect of microstructural composition of oxide scales on growth stresses. Their study revealed that the transition of the initial scale on the surface of $(Cr,Fe)_2O_3$ to a scale with increasing Cr and decreasing Fe content caused tensile stresses to develop. A decrease in atomic volume associated with the transition is the apparent explanation for the tensile stress development.

The formation of fresh oxides inside the scale itself can be an important source of compressive stresses in oxide scales. Jaenicke et al. [9] found that in the oxidation of copper, micro-cracking induced by the growth stresses provides pathways for gas migration. The availability of copper molecules results in the formation of fresh oxides within the scale. Since the new oxides have higher volume than the cracked volume, significant compressive stresses are developed.

Mismatch of the TCE between oxide coatings and substrates is the reason for thermal stress generation in the oxide coatings during cooling or heating [10]. Thermal stress is a function of the TCEs and temperature difference. In most cases, oxides have lower TCE values than metal substrates, and in such cases, cooling to room temperature from elevated temperature generates compressive stresses in the oxide coatings. Conversely, heating to high temperature develops tensile stresses in the oxide coatings. Thus tensile and/or compressive stresses are developed in the oxide coatings during thermal cycling. Moreover, along with temperature changes, phase transformations in both oxide coatings and substrates can result in a stress development. Different researchers have studied thermal cycling induced stresses in oxide

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coatings. For example, Christl et al. [11] incorporated acoustic emission techniques to detect thermal cycling induced oxide scale cracking on low alloy steel. In a different work, Zhang et al. [12] monitored scale cracking and spalling on Ni–30Cr alloys oxidized at 1000 °C and then cooled to room temperature either by natural furnace cooling or constant rate cooling.

In summary, during fuel cell operation, growth stresses in ever-thickening native scales on interconnects may degrade the interfaces between the native scales and the protective MCO coatings. With degraded interfaces, TCE mismatch between the native scales and MCO coatings can cause unexpected MCO coating spallation when the fuel cell stack is shut down and goes from high operating temperature to room temperature. As a consequence of coating spallation, the now-uncoated interconnects are exposed to the high temperature corrosive environments resulting in damage to interconnects and ultimately decreased power density of the fuel cell stack. Therefore, the effective service lifetime of interconnects is limited by cooling induced coating spallation. Estimating lifetimes of the MCO coating is essential to assess the reliability of interconnects for high temperature fuel cell applications.

Liu et al. [13] have applied an integrated experimental-finite element modeling approach to predict the life of metallic (Crofer 22) interconnects for SOFCs. Their methodology was based on measuring interfacial shear strength. But in previous work, Akanda et al. [6] suggested that the interfacial fracture energy is more related to the coating adhesion than is the interfacial shear strength. In the present study, an integrated experimental–analytical methodology based on interfacial fracture energy was implemented to estimate the effective lifetime of MCO coatings for a particular operating temperature. The key steps of the methodology are shown in Fig. 1 and are explained in the following points:

- In the experimental part, room temperature four-point bend experiments were performed on coated interconnects oxidized for different periods of time. An energy-based fracture mechanics approach was used to obtain the interfacial fracture energy. In addition to the interfacial fracture energy, interfacial shear strength could also be obtained from the experiments using a shear lag model.
- Coated interconnects had been oxidized at 900 °C for 100, 600 and 1000 h in order to quickly grow native scales of different thicknesses. It is known that the higher oxidation temperatures will produce natrive scales with a more porous bulk microstructure [14]. Nonetheless, the experimental results were then used to describe the evolution of room temperature interfacial fracture energy as a function of native scale thickness. Despite the different bulk microstructure, the reason for oxidizing the coated interconnects at higher temperature (900 °C) rather than the typical operating temperature of a fuel cell

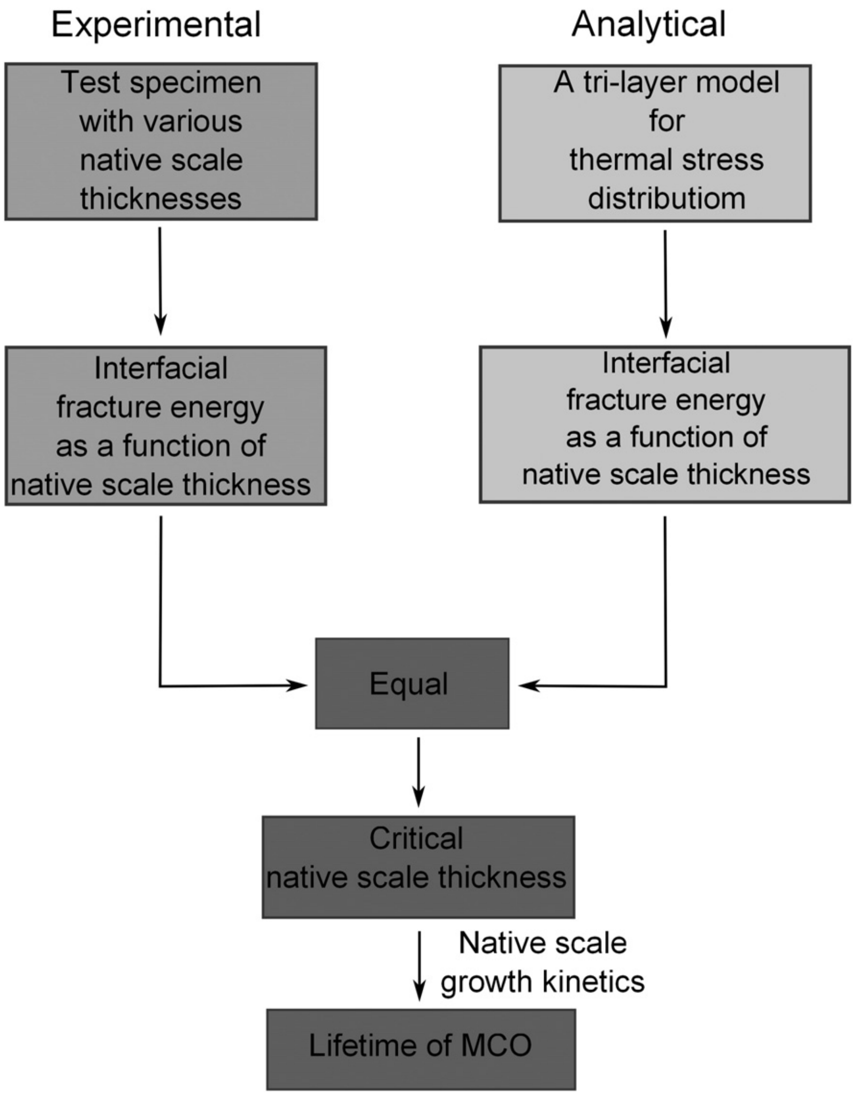

Fig. 1. Integrated experimental–analytical methodology to predict lifetime of MCO coatings on metallic interconnects.