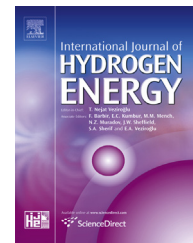


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Controlling chromium vaporization from interconnects with nickel coatings in solid oxide devices

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ABSTRACT

Vaporization of Cr-rich volatile species from interconnect materials is a major source of degradation that limits the lifetime of planar solid oxide devices (solid oxide fuel cells and solid oxide electrolysis cells) with metallic interconnects. Some metallic coatings (Ni, Co, and Cu) may significantly reduce the Cr release from interconnects and slow down the oxide scale growth on the steel substrate. To shed additional light upon the mechanisms of such protection and find a suitable coating material for ferritic stainless steel materials widely used for interconnects, we used a combination of first-principles calculations, thermodynamics, and diffusion modeling to investigate which factors determine the quality of the Ni metallic coatings. We found that Cr migration in Ni coatings is determined by a delicate combination of the nickel oxidation, Cr diffusion, and phase transformation processes. Although the formation of Cr₂O₃ is more exothermic than that of NiO, the kinetic rate of the chromia formation in the coating layer and its surface is significantly reduced by the low mobility of Cr in nickel oxide and in NiCr₂O₄ spinel. These results are in a good agreement with diffusion modeling for Cr diffusion through the Ni coating layer on the ferritic 441 steel substrate and available experimental data.

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Introduction

Metallic interconnects act as engineering barriers between anode and cathode gases and provide the electronic connection between the single cells in the stack of planar solid oxide fuel cells (SOFC) [1] and solid oxide electrolysis cells (SOEC) [2]. SOFCs devices produce electricity directly from oxidizing a

fuel, while SOECs produce oxygen and hydrogen gas in the process of steam electrolysis. These high temperature solid oxide devices place stringent requirements on materials used for the cell construction. In fact, appropriate materials for cell components are very scarce [3]. The most important consideration is the matching of the thermal expansion coefficients of electrode materials with that of the electrolyte to guarantee the high quality of the interfaces and to prevent cracking and/

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or delamination of the device components either during high temperature operation or heating/cooling cycles. Other technical requirements for these materials include a high resistance against oxidation and creep at temperatures 750–900 °C in aggressive environment (hydrogen, oxygen, water vapor, etc.) and a high electrical conductivity of the surface oxide scales.

Ferritic steels with chromium contents >20 wt.% and Cr based alloys were identified as the best materials for metallic interconnects because of their ability to form Cr₂O₃ scales that protect the material from rapid oxidation while retaining a reasonably high electrical conductivity [4]. However, these materials have tendency to release gaseous Cr species during solid oxide device operation [5,6]. These volatile Cr species are reduced at different locations of electrodes, electrolyte, and their interfaces and form Cr-rich phases [7] which inhibits the electrochemical processes in the cell. This effect is often called “Cr poisoning”; the corresponding degradation mechanisms of components of solid oxide devices with interconnects fabricated out of different Cr containing materials were proposed and extensively discussed in the previous publications [8–18].

Different metallic and metal oxide coatings may significantly slow down the Cr retention from stainless steel interconnects [19]. The best Cr retention capabilities were observed for alumina scales formed at the top of aluminum containing alloys. However, the high electrical resistance of alumina, which is five orders of magnitude higher than that of chromia [20], makes alumina forming alloys seemingly unsuitable as interconnect material. The TiO₂ layers formed on top of Nicrofer-7520 alloy turned out to be less effective as they were partially broken up and overgrown by Cr–Fe-spinel which could be the result of the porosity and the uneven morphology of the underlying Fe–Cr oxide.

Metallic coatings of Co, Cu and Ni are considered as promising coating materials for metallic solid oxide devices interconnects. The Co, Cu and Ni coatings showed a reduction of the Cr release by more than 2 orders of magnitude compared to the uncoated substrate material of Crofer 22 APU, or by about 3 orders of magnitude compared to pure chromia scales at 800 °C in humid air [19]. Even after 900 h or 1200 h of operation at 800 °C in humid air and 3–4 thermal cycles to room temperature no decrease of the Cr retention was observed. The SEM/EDX analyses shows, that the metallic Co, Cu, and Ni coatings were completely oxidized during the annealing at 800 °C in humid air, and the coating layers consisted of Co₃O₄, CuO and NiO, respectively. The literature values of the electrical conductivities for all of these oxides are 1–2 orders of magnitude higher than that of Cr₂O₃. Also, the oxidized metallic coatings formed effective barriers against oxidation of the substrate material. Advantages of metallic Co, Ni or Cu coatings are their low costs and easy and rapid fabrication by a wide range of techniques.

The aim of this study is to understand which properties of the coating systems are responsible for reducing the Cr vaporization from stainless steels used as interconnectors and the increase of the electronic conductivity of the interconnector by reducing the growth of sublayered chromia scales. For this purpose, we used a combination of first-principles calculations, thermodynamic, and diffusion

modeling for Cr behavior in oxidized and unoxidized Ni coating positioned on the top of stainless steel. We found that Cr migration through the coating film is defined by the two main competing factors: (i) high Cr solubility in unoxidized Ni matrix, and (ii) possible chromium and nickel oxides segregation in oxidized Cr–Ni alloys. Coating oxidation process significantly increases the resistance of the film to Cr migration and is crucially important for controlling the Cr species evaporation from Cr containing interconnects.

Brief review of thermodynamics and kinetics of oxidation of metallic materials

The minimization of Cr evaporation from a coated interconnect may be caused by one of the three reasons: (i) Cr diffusion through the coating layer takes a sufficiently long time; (ii) Coating layer gets oxidized itself and forms oxide(s) different from Cr₂O₃. The Cr migration rate through these oxides is different from the Cr migration rate in unoxidized metallic coating. In turn, this may slow down the formation of chromium oxide islands at the gas-coating interface and, therefore, slow down the release of gaseous Cr-bearing species; (iii) Complex oxides such as spinels may be formed because of solid state reaction between Cr₂O₃ and oxides formed in the coating layer which may bind Cr in a complex oxide layer and thereby prevent its migration to the gas-coating interface.

First, we investigated the oxidation thermodynamics of the coating materials. It was done using the ThermoCalc AB software version S (Stockholm, Sweden) [21], and the TTFE6 database. This software employs the so-called CALPHAD approach (CALculation of PHase Diagrams) allowing for conducting self-consistent evaluation of the thermodynamic properties of a given material, and the corresponding phase diagram [22–24]. We used it to compute the binary Fe–Cr–O and Ni–Cr–O isothermal cross-sections at 1073 K (800 °C) to assess the mutual solubility of Cr in Fe and in Ni in the presence of oxygen. One of our goals was to assess the values of the dissociation pressure for different oxides of interest. The so-called “dissociation pressure” for a given oxide (it is defined as the unique partial equilibrium pressure of oxygen gas at which the metal and its oxide coexist) is calculated for the A_mB_n oxide as follows [25]:

$$\Delta G_{A_m B_n}^0 = \frac{m}{2} RT \ln(p_{O_2}^{\text{diss}}) \quad (1)$$

In expression (1), R stands for the universal gas constant, T is the absolute temperature, and $\Delta G_{A_m B_n}^0$ is the standard Gibbs free energy of the formation of the corresponding oxide, A_mB_n. When deriving this expression, we took into account that the activities of the solid metal and its oxide are equal to unity [25]. In the modified Ellingham–Richardson diagram in Fig. 1, the values of the corresponding $\Delta G_{A_m B_n}^0$ were used to calculate the dissociation pressures for different oxides [26]. These values of $\Delta G_{A_m B_n}^0$ are not plotted in the figure. Instead, the dissociation pressure for the several oxides was plotted as a function of temperature [26]. If the oxygen pressure in the system is higher than the dissociation pressure of its oxide, then the metal surface will remain unoxidized. If the opposite case is realized, then the A_mB_n oxide will be stable.

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