DETERMINATION OF CHROMIUM VAPORIZATION RATES OF DIFFERENT INTERCONNECT ALLOYS BY TRANSPIRATION EXPERIMENTS

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ABSTRACT

Currently used interconnect materials, such as chromium-containing steels and chromium-based alloys (1), are protected from corrosion by a chromia scale. Under cathodic operating conditions of the Solid Oxide Fuel Cell (SOFC) this Cr$_2$O$_3$(s) layer is forming volatile chromium(VI) species at the surface of the alloy. The reduction of gaseous chromium(VI) species, mainly CrO$_3$(g) and CrO$_2$(OH)$_2$(g), at the cathode-electrolyte interface leads to precipitation of solid Cr(III) oxides and thereby to a degradation of cell performance. In this paper, the partial pressure of CrO$_2$(OH)$_2$(g), the most abundant volatile Cr(VI) species over Cr$_2$O$_3$(s), was determined for temperatures between 400 °C and 950 °C (in air with $p$(H$_2$O) = 0.02 bar). The enthalpy of reaction for the formation of CrO$_2$(OH)$_2$(g) was calculated and compared to the literature. In addition to this equilibrium studies with Cr$_2$O$_3$(s), non-equilibrium transpiration experiments under real cathodic SOFC conditions were carried out using uncoated and coated metallic interconnect materials. The chromium retention potential of protective ceramic scales like La$_{0.99}$Mg$_{0.16}$Al$_{0.12}$Cr$_{0.72}$O$_3$, deposited on metallic substrates by vacuum plasma spraying (VPS), was investigated.

INTRODUCTION

Typically used metallic interconnect materials form a Cr$_2$O$_3$(s) scale at the surface under cathodic operating conditions of the SOFC ($T$ = 850-950 °C, $p$(H$_2$O) = 0.02 bar, $p$(O$_2$) = 0.21 bar). Depending on water vapour pressure and temperature, different volatile chromium(VI) species are released from the Cr$_2$O$_3$(s) layer. In oxygen flow, CrO$_3$(g) is the dominating gaseous Cr(VI) species. In the presence of water and oxygen, CrO$_2$(OH)$_2$(g) is the most abundant volatile species over Cr$_2$O$_3$(s) (2). Electrochemical reduction of gaseous Cr(VI) species to solid Cr(III) oxides at the triple phase boundary cathode-electrolyte-oxidant leads to a rapid degradation of the electrical properties of the fuel cell.

In the literature, there are two different ways considered to be suitable to reduce chromium release from metallic interconnect materials: (I) Reduction of the operating temperature of the cell (2) and/or (II) Application of protective ceramic scales (3), either
formed by the interconnect material itself (4), or deposited on the metal substrate by a VPS coating process. Depending on the thermal expansion coefficient of the interconnect alloy, the composition of ceramic coating materials which are deposited on the substrate, has to be adjusted. On the oxide dispersion strengthened (ODS) alloy Cr5Fe1Y2O3 (metallic interconnect in the planar SOFC concept of Siemens), different acceptor doped lanthanum chromites were used as protective coatings with a scale thickness of ~30 μm.

The objective of this paper is the determination of chromium transport rates under both, equilibrium and non-equilibrium conditions by transpiration experiments. Equilibrium experiments were carried out with Cr2O3(s) powder. In the case of non-equilibrium studies, different interconnect alloy samples were used. The chromium transport rates obtained by equilibrium transpiration experiments were used to calculate the partial pressure of the most abundant volatile chromium(VI) species CrO2(OH)2(g) for temperatures between 400 °C and 950 °C (in air with p(H2O) = 0.02 bar).

Non-equilibrium transpiration experiments were carried out under realistic cathodic SOFC conditions (T = 850 °C or T = 950 °C, in air with p(H2O) = 0.02 bar) using different uncoated and coated interconnect samples. In the case of coated samples protective perovskite scales were applied on two substrate materials (the ODS alloy Cr5Fe1Y2O3 and the steel X10CrAl18 [Fe18Cr1Al0.1C]). The investigated perovskite compositions of the VPS layers were La0.9Sr0.1CrO3, La0.9Ca0.1CrO3, La0.8Sr0.2CrO3, and La0.99Mg0.16Al0.12Cr0.72O3. In addition to the vaporization studies, the microstructure of the coated interconnect samples was analyzed by scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) after each transpiration experiment.

**EXPERIMENTAL**

**Sample Composition and Size**

Transpiration experiments under equilibrium conditions were carried out with Cr2O3(s) powder (99 % purity, Fluka, Switzerland) to ensure saturation of the carrier gas by a large surface area. The Cr2O3(s) powder is kept in a quartz boat in the sample chamber of the transpiration apparatus (see 13 in Fig. 1).

Uncoated as well as coated samples which were used for non-equilibrium studies, had the dimensions L = 80 mm, W = 30 mm and H = 5 mm with rounded edges. The chromium transport rate of five different uncoated interconnect materials was determined: The ODS alloy Cr5Fe1Y2O3, the ferritic steel X10CrAl18, alloy 446 (Fe25Cr0.7Mn0.5Si), Fe20Cr5Al and the model alloy Fe24Cr0.8Mn0.3Ti0.3La (4).

Protective perovskite coatings of ~30 μm scale thickness were applied on the substrates Cr5Fe1Y2O3 and X10CrAl18 by a VPS process at DLR (Deutsche Luft- und Raumfahrt Gesellschaft), Stuttgart. The compositions of the coating materials deposited on the two metallic substrates were: La0.9Sr0.1CrO3, La0.9Ca0.1CrO3, La0.8Sr0.2MnO3, and La0.99Mg0.16Al0.12Cr0.72O3. Both, uncoated and coated specimens were kept in a quartz sample holder in the sample chamber of the transpiration apparatus.
Transpiration Experiments

The determination of chromium vaporization rates was carried out using the transpiration method. In the case of equilibrium studies with pure chromia, the vapour pressure of the most abundant gaseous chromium(VI) species CrO$_2$(OH)$_2$ (g) was calculated from the measured chromium vaporization rate. Figure 1 shows the transpiration apparatus, developed for the measurement of chromium transport rates under both, equilibrium and non-equilibrium conditions.

![Diagram of experimental setup](image)

Fig.1, Experimental setup developed for the measurement of chromium transport rates.

In a heated quartz tube, volatile chromium(VI) species are vaporized from the sample surface. A stream of carrier gas transports the gaseous species from the reaction tube to the condensing tube, which is cooled at room temperature. The reaction and condensing parts of the quartz tube are connected by a joint. A capillary is used to separate the two compartments of the tube. The temperature in the sample chamber is monitored by a Pt6%Rh/Pt30%Rh (type B) thermocouple. Diffusion effects in the sample chamber are minimized by the use of a quartz filter between the gas inlet and the reaction tube. The reaction gases enter the humidifier after passing the mass flow controller. The water vapour pressure is controlled by the temperature of a cooler. At the end of the transpiration experiment the condensing part of the quartz tube was washed with distilled water and conc. mineral acids. The chromium concentration of the solution was determined by atom absorption spectroscopy (AAS). The chromium transport rate was calculated from the amount of chromium released and the total flow of carrier gas measured with the mass flow controller.
Equilibrium studies with Cr$_2$O$_3$(s) powder as well as non-equilibrium transpiration experiments with interconnect samples were carried out in humidified synthetic air ($p$(H$_2$O) = 0.02 bar). In any cases, the flow rate dependence of the chromium transport rate was studied before starting the transpiration experiments. For measurements under equilibrium conditions a gas flow rate of $v = 150$ ml/min was considered to be suitable. In the case of non-equilibrium experiments a gas flow rate of $v = 1800$ ml/min was selected. Equilibrium transpiration experiments were carried out at six different temperatures between 400 °C and 950 °C, non-equilibrium experiments were done at temperatures of 850 °C or 950 °C. The uncoated interconnect alloys were pre-oxidized at temperatures of 800 °C, 850 °C or 1000 °C for durations between 100 h and 200 h. Chromium transport rates measured by non-equilibrium transpiration experiments with VPS-coated Cr$_5$Fe$_1$Y$_2$O$_3$ and X10CrAl18 specimens were compared to the results obtained for the uncoated substrates, in order to calculate the chromium retention of the protective scale. Moreover, the chemical composition and morphology of the protective scales were investigated by SEM/EDX, X-ray diffraction analysis (XRD) and chemical analysis after the transpiration study to reveal possible microstructural changes.

RESULTS

Equilibrium Studies on Cr$_2$O$_3$(s)

Equilibrium studies on pure chromia were carried out at a carrier gas flow of 0.15 l/min. The selection of the appropriate gas flow, maintaining equilibrium conditions, was done by investigating the chromium transport rate with respect to the gas flow rate (see Figure 2).

![Graph showing gas flow dependency of chromium transport rate at 950 °C and $p$(H$_2$O) = 0.1 bar](image.png)

**Fig. 2** Gas flow dependency of chromium transport rate at 950 °C and $p$(H$_2$O) = 0.1 bar
In Figure 2 the measured chromium transport rate is plotted as a function of the carrier gas (humid air, \( p(\text{H}_2\text{O}) = 0.1 \) bar) at a temperature of 950 °C. Obviously, gas flow rates between \( v = 100 \) and \( v = 400 \) ml/min are suitable to ensure equilibrium conditions in the sample chamber of the transpiration apparatus. For flow rates larger than 400 ml/min, the measured chromium transport rate is no longer proportional to the gas flow, that means in case of \( v > 400 \) ml/min it is not possible to maintain equilibrium conditions.

Transpiration experiments under equilibrium conditions were carried out using chromia powder samples at temperatures of 400 °C, 500 °C, 600 °C, 750 °C, 850 °C and 950 °C in humidified air \( p(\text{H}_2\text{O}) = 0.02 \) bar. The partial pressure of the most abundant volatile chromium(VI) species over \( \text{Cr}_2\text{O}_3(\text{s}) \) was derived from the measured chromium transport rates according to the ideal gas law. Figure 3 shows the experimental results for the temperature dependence of the chromium vaporization over \( \text{Cr}_2\text{O}_3(\text{s}) \).

![Fig. 3 Measured temperature dependence of chromium vaporization over \( \text{Cr}_2\text{O}_3(\text{s}) \) in air and calculation of \( p(\text{CrO}_2(\text{OH})_2) \) and \( p(\text{CrO}_3) \) according to the literature.](image)

In Figure 3 the partial pressures obtained by transpiration experiments are compared to partial pressures calculated for the gaseous chromium(VI) species \( \text{CrO}_2(\text{OH})_2(\text{g}) \) and \( \text{CrO}_3(\text{g}) \) using thermodynamic data from the literature. According to the Ivtanthermo (5) data base the gaseous chromium(VI) species \( \text{CrO}_2(\text{OH})_2(\text{g}) \) is expected to be dominating over \( \text{Cr}_2\text{O}_3(\text{s}) \) in the presence of water. The experimental results of the equilibrium studies are in good agreement with the calculated (Ivtanthermo (5), Ebbinghaus (6)) temperature dependence of \( p(\text{CrO}_2(\text{OH})_2) \), if the slope of the curve is considered. The
absolute values of \( p(\text{CrO}_2(\text{OH})_2) \), determined by transpiration experiments, are ten times bigger than the prediction according to Ivtanthermo (5) but ten times smaller compared to the Ebbinghaus (6) calculations. From the slope of the measured temperature dependence of the partial pressure \( p(\text{CrO}_2(\text{OH})_2) = p_c \) the following equation [1] was derived for the mean experimental temperature \( (T = 948 \text{ K}) \).

\[
\ln p_c(\text{Pa}) = -7387.5 \cdot T^{-1} + 0.442
\]  

[1]

Further calculations based on the slope of the determined temperature dependence of the chromium vaporization yielded the enthalpy of reaction for the formation of \( \text{CrO}_2(\text{OH})_2(\text{g}) \) over \( \text{Cr}_2\text{O}_3(\text{s}) \) in humid air. Using the van’t Hoff equation for the experimental results a value of \( \Delta H^\circ_{948} = 122.85 \text{ kJ/mol} \) was found for the enthalpy of reaction. From the Ebbinghaus (6) data a similar \( \Delta H^\circ_{948}(\text{calc.}) \) of 130.0 kJ/mol was calculated for the reaction of vaporization.

**Non-Equilibrium Transpiration Experiments with Uncoated Samples**

Non-equilibrium experiments were carried out with five different uncoated interconnect materials in humidified air \( (p(\text{H}_2\text{O}) = 0.02 \text{ bar}) \) at a flow rate of \( v = 1800 \text{ ml/min} \). The experimental temperatures were 850 \( ^\circ\text{C} \) or 950 \( ^\circ\text{C} \). In Table 1 the alloy compositions, the annealing times and the measured chromium transport rates are given. The composition of the model alloy HNA is approximately Fe24Cr0.8Mn0.3Ti0.3La (4).

| Interconnect Alloy | Cr5Fe1Y2O3 (ODS) | X10CrAl118 (1.4742) | Fe20Cr5Al (Fecralloy) | 446 | Model Alloy HNA (4) |
|--------------------|------------------|--------------------|----------------------|-----|---------------------|
| Temperature \( T/\circ\text{C} \) | 850 | 950 | 850 | 850 | 850 | 850 |
| Annealing Time \( t/\text{h} \) | 351 | 23 | 338 | 346 | 160 | 255 |
| Cr Transport Rate \( k/\text{ng m}^{-2} \text{s}^{-1} \) | 132.0 | 492.0 | 63.0 | 27.0 | 5.7 | 13.7 |

The results, listed in Table 1 reveal a high chromium transport rate for the chromium based ODS alloy Cr5Fe1Y2O3 and the chromium containing steel X10CrAl118. The reason for the slightly lower chromium transport rate found for X10CrAl118 is the formation of Fe-rich oxides on the surface of the alloy. The chromium activity in this mixed oxide scale is lower compared to the Cr activity in pure chromia formed on Cr5Fe1Y2O3.

The lowest chromium vaporization rates were found for the manganese containing materials 446 and HNA. These alloys form a Cr2MnO4 scale which reduces the vaporization of volatile Cr(VI) species (4). In case of alloy 446 a twenty times lower chromium transport rate compared to the chromia forming alloy Cr5Fe1Y2O3 was found (see Tab. 1). The alumina forming alloy Fe20Cr5Al showed a reduction of the chromium vaporization by a factor of five compared to the ODS alloy Cr5Fe1Y2O3. The source for
the release of volatile Cr(VI) species from the Fe20Cr5Al surface is the formation of Cr2O3(s) at the beginning of the pre-oxidation. Moreover it is possible that delamination and thereby local Al depletion due to internal oxidation is leading to chromia formation.

Non-Equilibrium Transpiration Experiments with Coated Interconnect Samples

The chromium vaporization rates of perovskite coated interconnect samples were determined in humid air at a flow rate of \( v = 1800 \text{ ml/min} \). Two different substrate materials (X10CrAl18 and Cr5Fe1Y2O3) were used at temperatures of \( T = 850 ^\circ \text{C} \) and \( T = 950 ^\circ \text{C} \). In Table 2 the investigated substrate/coating combinations as well as the experimental conditions and the results are listed. The calculated values of chromium retention were derived by comparing the Cr vaporization rates of coated (Table 2) and uncoated (Table 1) substrate materials.

| Alloy/Coating Combination | Temperature \( T/ ^\circ \text{C} \) | Annealing Time \( t/ \text{h} \) | Cr Transport Rate \( k/\text{ng m}^2 \text{s}^{-1} \) | Chromium Retention |
|--------------------------|-------------------|------------------|-----------------|------------------|
| Cr5Fe1Y2O3 (ODS)/ La0.9Sr0.1CrO3 (LSC) | 950 | 2006 | 4.58 | 99 % |
| Cr5Fe1Y2O3/ La0.9Sr0.1CrO3 | 850 | 847 | 1.72 | 99 % |
| X10CrAl18/ La0.9Sr0.1CrO3 | 850 | 346 | 4.72 | 93 % |
| Cr5Fe1Y2O3/ La0.9Ca0.1CrO3 (LCaC) | 950 | 736 | 13.6 | 97 % |
| X10CrAl18/ La0.8Sr0.2MnO3 (LSM) | 850 | 760 | 1.97 | 97 % |
| Cr5Fe1Y2O3/ La0.99Mg0.16Al0.12Cr0.72O3 | 950 | 1296 | 5.15 | 99 % |

Table 2 shows that the best results (of 99 % chromium retention) were obtained for the alloy/coating combinations Cr5Fe1Y2O3/La0.9Sr0.1CrO3 and Cr5Fe1Y2O3/ La0.99Mg0.16Al0.12Cr0.72O3 at a temperature of 950 ^\circ \text{C}. Also at a temperature of 850 ^\circ \text{C} the LSC coating on the Cr5Fe1Y2O3 sample yielded the highest chromium retention of 99 %. The reason for the higher chromium vaporization of coated X10CrAl18 substrates compared to coated Cr5Fe1Y2O3 samples is the change in the morphology of the different oxide scales: On Cr5Fe1Y2O3 samples, a thin, well adhering and homogenous Cr2O3(s) layer was observed. In the case of X10CrAl18 a porous, thick and delaminating mixed Cr/Fe oxide scale was found. This microstructure and a better adherence of protective perovskites on ODS result in a lower chromium vaporization rate and a higher chromium retention than X10CrAl18.
Another aspect is the difference in the thermal expansion coefficient of alloy and protective layer. For the alloy/coating combination X10CrAl18/LSM, the determined chromium retention is higher (97 %) than the retention obtained for the combination X10CrAl18/LSC (93 %). The reason is the bigger difference in the thermal expansion coefficient (Δα = 2-3 · 10⁻⁶ /K) of substrate and protective layer in the case of X10CrAl18/LSC. The thermal expansion coefficient of LSM and X10CrAl18 are matching better and less microcracks are found in the protective scale. Due to the better scale adherence, transpiration experiments with X10CrAl18/LSM yielded lower chromium vaporization rates than X10CrAl18 samples coated with LSC at a temperature of 850 °C.

Scanning electron microscopic investigations revealed the source of chromium vaporization from VPS-coated interconnect samples. Figure 4 shows the cross section of the Cr₅Fe₁Y₂O₉/La₀.₉₉Mg₀.₁₆Al₀.₁₂Cr₀.₇₂O₃ specimen after treatment for t = 1296 h at a temperature of T = 950 °C in humid air.

![Fig. 4, Cross section of Cr₅Fe₁Y₂O₉/La₀.₉₉Mg₀.₁₆Al₀.₁₂Cr₀.₇₂O₃ sample after t = 1296 h of transpiration experiment at 950 °C in humid air (p(H₂O) = 0.02 bar)](image)

In Figure 4, a Cr₂O₃(s) sublayer between the VPS coating and the ODS substrate is observed and identified by EDX and XRD analysis. Obviously this chromia sublayer is releasing volatile chromium(VI) species in transpiration experiments under real cathodic SOFC conditions (air, p(H₂O) = 0.02 bar, T = 950 °C, v = 1800 ml/min).

In addition to SEM investigations aiming at the source of chromium vaporization, the pathway of chromium transport through the protective perovskite scale was studied. The morphology of the VPS layer was analyzed subsequently by SEM and EDX after different durations of the transpiration experiments. In Figure 5, the measured chromium vaporization rates for the sample ODS/LSC are plotted versus the annealing times of the experiments at T = 950 °C in humidified air. Figure 6a and 6b show the change in morphology of a La₀.₉Sr₀.₁CrO₃ layer on an Cr₅Fe₁Y₂O₉ substrate before and after a transpiration experiment of 1359 h at a temperature 950 °C in humid air. The observed densification process is considered to be the reason for the time dependence of the vaporization (Fig. 5).
Fig. 5, Time dependence of Cr vaporization of Cr$_5$Fe$_1$Y$_2$O$_3$/La$_{0.9}$Sr$_{0.1}$CrO$_3$ at 950 °C

Fig. 6, (a) Cr$_5$Fe$_1$Y$_2$O$_3$/La$_{0.9}$Sr$_{0.1}$CrO$_3$ sample as received and, (b) after 1359 h of annealing at a temperature of $T = 950$ °C in humidified air.

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SUMMARY AND CONCLUSION

Equilibrium studies on pure Cr₂O₃(s) were carried out to determine the temperature dependence of the partial pressure of the most abundant volatile chromium(VI) species. The measured temperature dependence of \( p(\text{CrO}_2(\text{OH})_2) \) was in good agreement with calculations based on literature data of Ebbinghaus (6) and Ivтанthermo (5) if the slope is considered. The absolute pressures \( p(\text{CrO}_2(\text{OH})_2) \) were lying between the Ivтанthermo (5) prediction and the Ebbinghaus (6) calculation with a deviation of one order of magnitude. For the formation of \( \text{CrO}_2(\text{OH})_2(g) \) over \( \text{Cr}_2\text{O}_3(s) \) in the presence of oxygen and water the enthalpy of reaction was determined to be \( \Delta H^\circ_{948} = 122.85 \text{ kJ/mol} \) at the mean experimental temperature of 948 K, according to Ebbinghaus (6) a similar value of \( \Delta H^\circ_{948} = 130.0 \text{ kJ/mol} \) was calculated.

Non-equilibrium transpiration experiments with uncoated interconnect samples at a temperature of 850 °C showed the lowest chromium vaporization rates for the manganese containing alloys 446 and HNA (4). Obviously, the formation of \( \text{Cr}_2\text{MnO}_4(s) \) at the surface of the substrate is leading to a decrease of chromium vaporization. The spinel formation on HNA is yielding a twenty times lower chromium vaporization rate compared to the chromia forming ODS alloy. A chromium retention of 99 % was found in transpiration experiments with VPS-coated metallic substrates. Among the investigated substrate/coating combinations the lowest values for the chromium retention were obtained for ODS/La\(_{0.99}\)Mg\(_{0.16}\)Al\(_{0.12}\)Cr\(_{0.72}\)O\(_{3}\) and ODS/LSC. SEM investigations of the morphology of protective perovskite scales revealed a time dependence of chromium release due to a densification process in the VPS layers.

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