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Temperature dependence of corrosion of ferritic stainless steel in dual atmosphere at 600–800 °C

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HIGHLIGHTS

- Breakaway corrosion occurs when a steel is exposed to dual environment of air/H_2.
- Passive layers forms on reference samples in air only.
- There is an inverse temperature dependence of the dual atmosphere effect.

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ABSTRACT

The ferritic stainless steel AISI 441 (EN 1.4509) is exposed for 1000 h to air - 3% H_2O on one side and to Ar - 5% H_2 – 3% H_2O on the other at temperatures 600, 700, and 800 °C. Conditions are chosen to mimic the environment of metallic interconnects in an operating solid oxide fuel cell (SOFC). At 600 °C, ~25 µm thick Fe_2O_3/$(Fe,Cr)_3O_4$ forms on large parts of the air side of the samples. Reference samples exposed to air - 3% H_2O on both sides form thin protective layers of $(Cr,Mn)_3O_4$/Cr_2O_3 at the same temperature. At higher temperatures, 700 and 800 °C, all samples form protective layers of $(Cr,Mn)_3O_4$/Cr_2O_3 regardless of exposure to single or dual atmosphere. It is concluded that corrosion resistance in a dual atmosphere has an inverse dependence on temperature. Different hypotheses for the underlying cause for the dual atmosphere effect are discussed and compared to the experimental data.

1. Introduction

Solid oxide fuel cells (SOFC) are high-efficiency energy conversion devices that, due to their high operating temperature of 500–900 °C, are able to run on a variety of different fuels. These fuels range from hydrogen to hydrocarbon gases, like natural gas and reformate gas. The most common way to build SOFC units is to connect individual planar cells in series to create a fuel cell stack of up to 100 cells, depending on the power requirements. The modular nature of the fuel cell stack makes it a very scalable technology, which allows for designing systems with power capacities ranging from a few hundred watts up to megawatts. The individual fuel cells within a stack are separated by metallic interconnects, which also provide electrical contact between each cell.

Interconnects are generally made of ferritic stainless steels due to their thermal expansion coefficient (TEC), which matches the other cell components, in combination with good formability and electrical conductivity at a reasonable cost. For these steels, corrosion resistance is achieved by the formation of a chromium oxide layer on the steel surface, which acts as a diffusion barrier and slows down the oxidation of the steel part. For interconnects, it is important that the protective chromia layer is well adherent to avoid loss of electrical contact, and that the layer is slow growing since a thicker chromia layer leads to higher ohmic losses [1]. Furthermore, chromium should preferably be oxidized over iron, since iron oxide grows several orders of magnitude faster than chromium oxide and, thus, offers poor corrosion protection. The ability of a steel to form a protective chromia scale is affected by many factors, such as the concentration of Cr in the steel, the alloy microstructure, the surface treatment, and by minor alloying elements [2]. The preferential oxidation of chromium in a stainless steel is also greatly affected by the environment to which it is exposed. For instance, stainless steels in atmospheres with a high steam content are known to be prone to form iron oxide when they would otherwise form protective chromia scales in atmospheres of air at the same temperature [3]. In SOFC stacks the interconnects are exposed to high pO_2 on the oxidizing side and to low pO_2 on the fuel side and conduct electric current in the range of 0.1–1 A cm^{-2}. It has been shown that electric current can

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affect the oxidation of ferritic stainless steels. In general, the oxidation rate is reduced on the cathode side and increased at the anode side [4–6] but accelerated corrosion, with iron nodule formation, on both the anode and the cathode has also been reported [7].

Several researchers have shown, in the context of SOFCs, that when exposed to hydrogen on one side and air on the other side, ferritic stainless steel sheets tend to form more iron oxide on the air side than when only exposed to air or hydrogen atmospheres [8–15]. Similar findings have also been reported in the context of steam and flue gas tubes, in which corrosion was found to be accelerated on the air side of the tubes [16,17]. It should be noted that the magnitude of the reported effects varies significantly between different studies. E.g. Kurokawa et al. [18] and Ardigo et al. [7] do not observe accelerate oxidation under dual atmosphere conditions. This disagreement is probably due to experimental differences, such as hydrogen concentration, pretreatment of sample as well as alloy composition.

The dual atmosphere effect, i.e. promotion of iron oxide on the air side, is likely caused by the diffusion of hydrogen through the steel substrate, which interferes with the oxidation process on the air side of the sample. It has been shown that hydrogen can diffuse relatively fast through a steel sheet and at 600 °C a permeation rate in the order of mm h^{-1} can be expected [19]. Skilbred and Haugsrud have found increased hydrogen content in the oxide scale of the air side of a dual-atmosphere-exposed ferritic stainless steel at 800 °C [20]. The flux of hydrogen is initially expected to be determined by the steel thickness, but after oxidation and formation of a Cr_2O_3 scale the flux quickly becomes rate limited by the chromia thickness. Kurokawa et al. measured four orders of magnitude lower permeability for hydrogen in the oxide scale formed on Fe16Cr compared to the hydrogen permeability in ferrite at 800 °C [21]. The mechanism for how hydrogen affects the air-side oxide scale is unknown. Yang et al. have suggested altered defect chemistry of the protective chromia scale due to doping with hydrogen, which leads to an increase in metal ion diffusivity [8]. Holcomb et al. have suggested that steam formation within the oxide results in pore formation that offers fast transport of oxygen, which leads to accelerated corrosion [10]. Other findings that might explain the dual atmosphere effect are:

- Increased internal oxidation, which causes the immobilization of Cr and results in the depletion of Cr near the metal oxide [22].
- Formation of hydroxides on oxygen sites in the oxide lattice, which allows for faster oxygen diffusion due to the smaller ionic radius of the hydroxides compared to oxygen ions [23].

Most studies on the oxidation of ferritic steels in dual atmospheres have been carried out at temperatures of around 800 °C. In a previous study, we exposed the ferritic stainless steel AISI 441 to a dual atmosphere at 600 °C and found a strong dual atmosphere effect [14]. Local iron oxide nodules of up to 25 μm thickness were found on the air side of the samples exposed for 1000 h to humid air on one side and to humid hydrogen on the other. In contrast, the samples exposed to humid air on both sides formed protective scales with a thickness in the order of a few hundred nm, consisting of chromia and chromium manganese spinel. The strong dual atmosphere effect at the relatively low temperature of 600 °C led to the suspicion that the dual atmosphere effect might have an inverse relation to temperature, meaning that thicker oxide scales are formed at lower temperatures. Such inverse temperature dependence has been reported for ferritic steels exposed to a single atmosphere of humid hydrogen [24] and when exposed to a flow of humid air [25]. In both studies the authors explained this by a change of the oxidation mechanism. It is suggested that due to an insufficient flux of Cr from the alloy towards the metal/oxide interface the chromia scale growth cannot be maintained and non-protective Fe rich oxide is formed instead. In the paper by Jonsson et al. [25] this transition to a non-protective regime is explained by Cr depletion caused by the formation of gaseous $CrO_2(OH)_2$ in the presence of water vapor (see Equation (1)) [26].

Table 1
Composition in wt% of the specific batch of AISI 441 used in this study, provided by Sandvik Materials Technology.

Material	Fe	Cr	Ni	Mn	Si	Ti	Nb	C	P	S
AISI 441	Bal	17.7	0.19	0.30	0.55	0.15	0.37	0.015	0.027	0.002

$$\tfrac{1}{2}Cr_2O_3(s) + \tfrac{3}{4}O_2(g) + H_2O\,(g) = CrO_2(OH)_2(g) \qquad (1)$$

The aim of the current study is to investigate the temperature dependence of the dual atmosphere effect by exposing the ferritic stainless steel AISI 441 at different temperatures, using the same experimental setup and ferritic stainless steel as in the previous study at 600 °C [14].

2. Experimental

Circular specimens with 20 mm diameter were cut from 0.2 mm thick AISI 441 foil and were cleaned with acetone and ethanol in an ultrasonic bath. No further surface treatment was performed on the steel. The surface finish of the steel was bright-annealed with a roughness of 0.1–0.3 μm, according to Sandvik Materials Technology, which provided the material. The composition of the AISI 441 ferritic stainless steel used is given in Table 1. To simulate SOFC stack production, where the stack is usually initially heated to a higher temperature in air, the samples were pre-oxidized at 800 °C in ambient atmosphere for 3 h before exposure to dual atmosphere, and the mass change after pre-oxidation was recorded. The samples were placed in a 253 MA steel holder, based on a design from National Energy Technology Laboratory [10,11,27], which allows for separate control of gas composition, including humidity, and gas flow on each side of the samples. Gold gaskets were used to seal the ferritic stainless steel samples to the holder, and gas tightness was controlled regularly. The humidity level was checked using a chilled mirror humidity sensor (Michelle – Optidew Vision). The sample holder was placed in a horizontal tube furnace (60 mm diameter). A heating/cooling rate of 5 °C min^{-1} was used and the setup was flushed for at least 12 h before heating was initiated. For more details on the experimental setup and sample holder, see Ref. [14].

Duplicate samples were tested in each experiment in which one set of samples was exposed to air on one side and to humid hydrogen on the other side. This will hereinafter be referred to as “dual atmosphere”. Another set of samples was used as references and was exposed to air on both sides, and this will be referred to as “single atmosphere”. The gas flow rate, gas contents, and temperature in the experiments carried out in this study are listed in Table 2. Exposures were conducted at temperatures of 600 °C, 700 °C, and 800 °C in high-flow humid air. A humidity of 3% was used to promote formation of volatile $CrO_2(OH)_2$ [28] and to replicate standard simulated SOFC cathode conditions of our laboratory [29]. The flow rates for the air were chosen to achieve an average flow speed of approximately 27 cm s^{-1} and were calculated from the dimension of the inside and outside (silica tube diameter) of the sample holder. Based on a previous study, this rate should be in a

Table 2
Conditions used in the experiments.

Temp.	Outer gas	Inner gas 1 (dual atmosphere)	Inner gas 2 (single atmosphere)
600 °C	8800 sml min^{-1} air – 3% H_2O	100 sml min^{-1} Ar - 5% H_2 – 3% H_2O	400 sml min^{-1} air – 3% H_2O
600 °C	600 sml min^{-1} air	100 sml min^{-1} Ar - 5% H_2 – 3% H_2O	50 sml min^{-1} air
700 °C	8800 sml min^{-1} air – 3% H_2O	100 sml min^{-1} Ar - 5% H_2 – 3% H_2O	400 sml min^{-1} air – 3% H_2O
800 °C	8800 sml min^{-1} air – 3% H_2O	100 sml min^{-1} Ar - 5% H_2 – 3% H_2O	400 sml min^{-1} air – 3% H_2O