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THE OXIDATION OF HIGH CHROMIUM CONTAINING ALLOYS IN SIMULATED SOLID-OXIDE FUEL-CELL ATMOSPHERES

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ABSTRACT

Four commercial ferritic alloys, IT-11 (Plansee SE), *Crofer22APU* (Krupp VDM), *F17TNb* and *F18TNbY* (ArcelorMittal) were selected and evaluated for oxidation behaviour under conditions relevant to solid-oxide fuel-cells (SOFC) and scale conductivity. Isothermal and cyclic oxidation tests were carried out at 800-900°C up to 3000 h. Impurities in the alloys, particularly Al and Si, were found to have a significant effect on oxide scale adherence and area specific resistance (ASR) of the scales. In the presence of rate-earth elements (La and/or Y), the adhesions of the chromia scale is improved and the oxidation rate decreased. It was found that Mn and Ti additions both have a significant effect on scale growth on the high chromium alloys in cathode and anode gases. Alloys containing Mn formed an outer layer of $(Mn,Cr)_3O_4$ above the chromia scale. The oxidation tests of commercial alloys show that an oxide scale growth is significantly dependent upon the anode gas composition. The oxide scales on the alloys were thicker in the H_2-CO-CO_2-H_2O mixture that in the carbon-free anode gas. However, the high chromium content in the alloys was helpful in resisting metal carburisation. The powder metallurgy alloy (*IT-11*) and *F18TNbY* steel with Y_2O_3 coating showed higher oxidation resistance and lower ASR in both anode and cathode gases. The tested alloys have acceptable properties for interconnect materials for solid oxide fuel cells.

1. INTRODUCTION

One of the challenges in improving the performance and low-cost of solid oxide fuel cell (SOFCs) is the development of suitable interconnect materials. The interconnect provides electrical connection between anode of the cell to the cathode of the neighbouring one and also separates the fuel and the air. Therefore the interconnect must be have high oxidation resistance and the oxide scales must have low area specific resistance in both anode and cathode atmospheres. Recent research has shown that the Fe-Cr based alloys are the best candidate materials for interconnect. Ferritic steels have good compatibility (e.g., similar coefficient of thermal expansion) with the ceramic components of the SOFC. It is well known that addition of small amount of Y and/or La can significantly improve the oxidation resistance of Fe-Cr based alloys. The incorporation of these elements can be made during metallurgical preparations (melt or powder) as well as through a surface diffusion treatment. In fact, both *IT-11*(Plansee SE) and Crofer*22APU* (Krupp VDM) contain Y and La for this purpose, which are added during metallurgical production. The Y_2O_3 coating was deposited on *F18TNb* by Chemical Vapour Deposition (CVD) technique in order to form a perovskite scale at high temperature. This paper reports on the oxidation behaviour of *IT-11*, *Crofer22APU, F17TNb* and *F18TNbY* under conditions relevant to SOFC. Further, the effectiveness of a Y surface treatment on enhancing oxidation resistance is presented.

2. EXPERIMENTAL PROCEDURE

Two commercial steels, *Crofer22APU* (Fe-22Cr-0.5Mn) and *F17TNb (*Fe-18Cr-0.5Mn) and powder metallurgical alloy, *IT-11* (Fe-26Cr-0.1Mn) as well as yttrium surface treated ferritic steel (*F18TNbY*) were tested in different anode gases and air at 800-900°C. The oxide scale morphologies were investigated using scanning electron microscopy (SEM) with an energy dispersive X-ray spectroscopy (EDS). Generally, back-scattered electron (BSE) images were used during the cross-section investigations in the SEM. The electrical resistances of the pre-oxidized alloys were measured below the temperature at which the pre-oxidation was carried out. The surface of the pre-oxidized sample was covered by platinum paste followed by placing platinum meshes on top of the pastes as current collectors. The experimental details have been described in ref. [1].

3. RESULTS AND DISCUSSION

The oxidation tests in simulated anode (Ar-4%H_2-2%H_2O) and cathode gases (air) are presented in Fig. 1. The weight gains for Ferritic steels (*Crofer22APU* and *F17TNb*) are similar in both atmospheres. The powder metallurgy alloy

(*IT-11*) had higher oxidation resistance than the other tested materials.

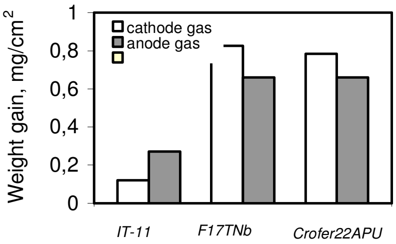

Figure 1: Weight gain of samples after 3000h oxidation in simulated anode and cathode (air) gases at 800°C.

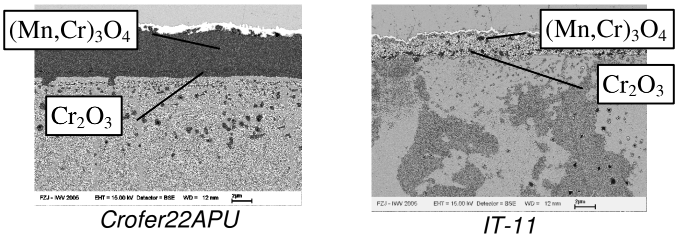

Figure 2: Oxide scale microstructures on Fe-Cr alloys after 3000h oxidation in Ar-4%H$_2$-2%H$_2$O at 800°C.

The oxide scales on the tested alloys had a duplex microstructure with a top layer consisting mainly of $(Mn,Cr)_3O_4$ spinel. The bottom layer in these scales consists of Cr_2O_3. The formation of $(Mn,Cr)_3O_4$ spinel on the surface is typical of Mn containing Fe-Cr based alloys, and it is due to the high diffusion coefficient of Mn in Cr_2O_3. The $(Mn,Cr)_3O_4/Cr_2O_3$ ratio in the scale depends on the Mn content in the alloys, gas compositions and the test temperature. Figure 2 presents SEM cross-sections of *Crofer22APU* and *IT-11* after exposure in simulated anode gas at 800°C. The specimen with high Mn content (*Crofer22APU)* exhibited higher $(Mn,Cr)_3O_4/Cr_2O_3$ ratio than that Mn poor powder metallurgy alloy (*IT-11*). Also Figure 2 indicates some internal Ti oxidation below the chromia layer. Possibly these oxide particles make the transition in thermal expansion coefficient between the oxide scale and the metal substrate more gradual, thereby reducing the shear stress in the interface which can cause spalling of the scale.

The contact resistances of the oxide scales were measured at different temperatures (alloys oxidized for 400 h at 800°C). Figure 3 shows that all alloys have significantly lower contact resistances at 800°C than at, for example 600°C. The highest value of approximately 60 $\mu\Omega \cdot cm^2$ was obtained for the *F17TNb* alloy at 600°C. The lowest contact resistances were found in the ferritic steel *IT-11* at all temperatures. The difference between the contact resistances, in this case, is due primarily to differences in scale thickness and composition. The highest electrical resistances are for ferritic steel (*F17TNb)* containing Si. Although the amount of Si in this alloy (0.6 wt.-%) is not sufficient to form a continuous internal layer of SiO_2, the scale contact resistivity is substantially increased.

The additional oxidation experiments in a carbon containing anode gas were carried out to obtain more detailed information concerning differences in the oxidation behaviour of the Fe-Cr based alloys.

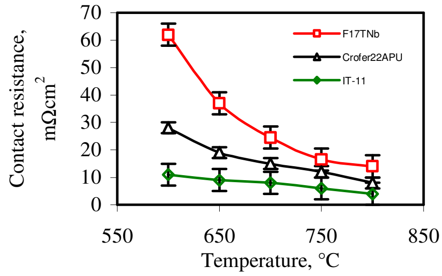

Figure 3: Contact resistance of oxide scales on tested alloys after 400 h oxidation at different temperatures simulated cathode gas.

A substantial influence of H_2O and CO/CO_2 contents on the oxidation rate of the *IT-11* alloy was observed (Fig. 4). The higher parabolic rate constants in carbon containing gas may also be related to the effects of high water vapour (18.5wt.-%) during initial establishment of the chromia scale.

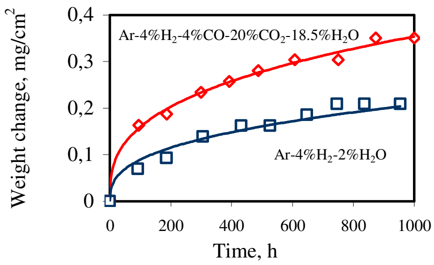

Figure 4. Oxidation behaviour of powder metallurgy alloy (*IT-11)* in different anode gases at 800°C.

The effectiveness of a Y surface treatment on enhancing oxidation resistance of ferritic steel is presented in Figure 5.

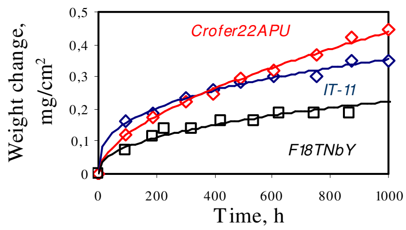

Figure 5. Oxidation behaviour of different alloys in carbon containing anode gas at 800°C.

The *F18TNbY* steel with Y_2O_3 coating showed extremely low oxidation rate compared with other tested non-coated alloys.

SUMMARY

The effectiveness of Y- surface modification on improving oxidation resistance of ferritic steels was demonstrated. All the tested alloys have acceptable properties for interconnect materials for solid oxide fuel cells.

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