FERRITIC STEEL INTERCONNECT FOR REDUCED TEMPERATURE SOFC

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ABSTRACT

Fe-Cr model alloys with variations in chromium content and additions of different reactive elements were studied for potential application in reduced temperature solid oxide fuel cells (SOFC). The oxidation resistance in both, anode and cathode atmospheres at 800°C were determined. Additionally, in-situ studies were carried out to characterize the high temperature conductivity of the oxide scales formed under these conditions. Based on these results, two model steels and a commercial ferritic steel were selected for further studies. Initial investigations of oxide scale formation, oxide conductivity, formation of volatile species, thermal expansion coefficient and compatibility with contact materials showed that these steels are potentially suitable as construction materials for the SOFC interconnect.

INTRODUCTION

Solid Oxide Fuel Cells (SOFC) comprise a number of components, i.e., anode, electrolyte, cathode and interconnect, each one made from a different material, with different physical and electrical properties. One of the critical components of SOFCs is the interconnect, which provides the electrical connection between the single cells and separates the anode and the cathode gases. The materials to be used as interconnect must possess:

• high temperature oxidation resistance in both anode and cathode atmospheres,
• good electronic conductivity of the oxide scales,
• a coefficient of thermal expansion (CTE), similar to that of the electro-active ceramic materials,
• a negligible tendency to interfacial reactions with the adjoining components,
• low cost and easy manufacturing.

In planar SOFC stacks which are operating at relatively low operating temperatures of around 800°C, oxidation resistant alloys are attractive alternatives for ceramic
As chromia-forming alloys possess high oxidation resistance at the operating temperatures, these materials are potentially suitable for interconnect applications. Alumina-forming alloys are less attractive for this application because the protective alumina scales formed during service have a very high electrical resistance. Of the chromia-forming alloys, those based on Ni are not attractive, since their CTE differ from that of the ceramic materials. Therefore, numerous studies have been focused on Fe-Cr based alloys which exhibit a good balance between oxidation resistance, electrical conductivity of the oxide scale and coefficient of thermal expansion.

One important problem that must be considered in the case of chromium containing alloys is cell degradation due to the formation of volatile chromium oxides and hydroxides at the cathode side. A reduction of the evaporation rate can be achieved by applying a protective coating or by using a steel that forms an oxide layer on top of the chromia scale. In a previous study it was shown that such duplex oxide layers can be obtained by suitable additions of Mn.

In the present study, the oxidation behaviour of FeCrMn steels, with and without addition of La/Ti, as well as the commercial alloy 446 have been studied in air and Ar/4%H2-2%H2O. Main emphasis was put on scale formation mechanisms and long term oxidation behaviour. The oxide scale properties were characterized in respect to composition, morphology, adherence and electrical resistance.

**EXPERIMENTAL DETAILS**

Fe-Cr model alloys with variations in chromium content between 16 to 25 wt% and additions of Ti and/or Mn as well as additions of oxygen active elements, such as La, Ce, Zr and Y, were produced by induction melting in a water-cooled copper crucible under an argon atmosphere. For oxidation studies, samples with nominal dimensions 20x10x2 mm were cut from the cast ingots and subsequently ground to 1200 grit surface finish and cleaned in acetone. The oxidation tests were carried out at 800°C in air and in Ar/4%H2-2%H2O. The experiments were interrupted at regular time intervals (250 h) for weight measurements. The oxide scales formed during the exposure in both atmospheres were investigated by light microscopy, scanning electron microscopy (SEM) with energy dispersive X-Ray analysis (EDX) and by X-ray diffraction (XRD). The in-situ electrical conductivity measurements were carried out at 800°C in air using a conventional four-point method. For these experiments, 10x10x2 mm samples were pre-oxidized for 100 h at 800°C in air. Then a layer of Pt paste was applied to both sides of the specimen. For the electrical connection a Pt mesh was used.

**RESULTS AND DISCUSSIONS**

Figure 1 shows the oxidation behaviour and microstructure of the scales on the various model alloys after exposure at 800°C in air. In respect to the weight change, the alloys could be divided into three groups,
• the alloys with small additions of oxygen active elements showed the lowest oxidation rates. The smallest weight changes were found for the alloy with La addition. The rapid incorporation of the oxygen active element into the scale has been shown to be a necessary requirement for obtaining an optimum reduction in the growth rate of the chromia scale (11) (Figure 1a).

• Mn additions led to a slight increase of the scale growth rate. However, this addition resulted in the formation of a (Mn,Cr)\textsubscript{3}O\textsubscript{4} spinel layer on top of the chromia scale (Figure 1b).

• Ti additions to Fe-Cr steels led to a higher growth rate of the oxide, mainly due to the formation of internal oxides of this element (Figure 1c).

In Figure 2a, the electrical resistances of the oxide scales during exposure up to 500 h in air at 800°C are shown. These results are compared with those for a typical ceramic (La,Sr)CrO\textsubscript{3} interconnect of 5mm thickness (7) and chromia-forming alloys Fe\textsubscript{25}Cr\textsubscript{La} and Fe\textsubscript{25}Cr\textsubscript{Zr}. In all cases, high electrical resistances were observed during the early stages of the test. The reason for this effect is not completely understood but is probably related to the initially poor electrical contact between Pt-paste and the non-ideally flat oxide surface (Figure 2b). After reaching stable conditions, all tested alloys showed lower electrical resistances than the ceramic interconnect. Comparing these results with the oxide scale composition and the weight change curves, shown in Figure 1, it is obvious that there are no direct correlations between electrical resistance and the scale thickness; the very thin chromia scale formed on FeCr alloy containing La showed a similar electrical resistance to that on a Mn containing alloy, which formed an outer spinel layer, and slightly higher electrical resistance than that of a (Mn,Cr)\textsubscript{3}O\textsubscript{4}/Cr\textsubscript{2}O\textsubscript{3} forming alloy containing Ti and La. Generally, it can be said that the alloys containing Ti and La exhibited relatively low electrical resistance. This is in agreement with studies concerning contact resistances of compounds between metallic material and ceramic, perovskite-type contact layers (12).

Long term oxidation studies in air and in Ar/4%H\textsubscript{2}-2%H\textsubscript{2}O were carried out for the Mn-containing alloys with Ti and La additions and for the Mn-containing commercial alloy 446. The results of these oxidation tests are shown in Figure 3. The weight change of the alloy containing Ti and La appeared to be similar in both air and Ar/4%H\textsubscript{2}-2%H\textsubscript{2}O atmospheres. In contrast, the alloys that do not contain these elements exhibited a higher oxidation resistance in Ar/4%H\textsubscript{2}-2%H\textsubscript{2}O than in air. SEM cross-sections show that the thickness of the scales formed on the various alloy were significantly differed (Figure 4).

In air, alloy 446 showed a relatively dense scale with good adhesion to the alloy but in Ar/4%H\textsubscript{2}-2%H\textsubscript{2}O, the scale formed had many pores and cracks. Also, the surface exhibited a wavy contour indicating a relaxation of the thermally induced stresses by plastic deformation of the substrate (13). After long term oxidation in air, an amorphous Si oxide sub-scale was found at the scale-alloy interface (Figure 4). This oxide increased the electrical resistance of the oxide scale. The scales formed on the Fe25CrMn model steels are relatively thin in both atmospheres, however, they tend to exhibit void formation, especially during air oxidation. It was detected by XRD (Figure 5) that these steels formed MnO in Ar/4%H\textsubscript{2}-2%H\textsubscript{2}O, which possessed a high electrical resistance. Both effects might have a significant influence in SOFC applications, in respect to
contact resistance and stability of the interface with the contact materials. The Ti- and La-containing steels seemed to exhibit the best performance, the oxide scales possessing similar thickness but better compactness and adherence in both atmospheres than the scales formed on the other two alloys (Fe25CrMn and alloy 446). Also fine precipitation of internal titanium oxides were visible.

Taking into account the results of the oxidation and contact resistance studies, it can be concluded that alloys of the type Fe25CrMn and Fe25CrMn (Ti,La) are promising materials for applications as interconnect in planar SOFCs, especially the alloy with Ti and La additions, in contrast to the commercial alloy 446. The Si in the latter alloy led to the formation of a Si-oxide sub-scale that increased the electrical resistance of the scale and tend to cause spallation of the oxide, as was mentioned above.

Figure 6 shows the coefficient of thermal expansion (CTE) of different materials currently used in planar SOFC stack designs, i.e., cathode (LaSrMnO3), anode substrate (Ni/8YSZ), electrolyte (8YSZ), compared with the potential interconnect materials and with a commercial ferritic steel, 1.4742, which has been commonly used as interconnect in previous SOFC designs. The alloys Fe25CrMn and alloy 446 have CTEs close to that of the anode material (Ni/8YSZ), whereas the ferritic steel Fe25CrMn (Ti,La) has a CTE comparable with that of the cathode and anode substrate. In contrast, the commercial steel 1.4247, possesses a thermal expansion coefficient which is substantially higher than that of anode and electrolyte materials.

Based on the results obtained from the thermal expansion experiments, two (Mn,Cr)3O4 spinel forming steels were selected for the determination of chromium evaporation rate by transpiration experiments. Initial results (14) have confirmed the assumption made above that the evaporation of volatile chromium species in case of MnCr2O4 spinel forming alloys was lower than for a pure chromia forming alloy (such as the ODS alloy Cr5Fe1Y2O3 or the commercial ferritic steel 1.4742).

CONCLUSIONS

Ferritic steels with high chromium contents with suitable additions of manganese and reactive elements and very low amounts of Al and/or Si, seem to be potentially suitable as construction materials in planar SOFC designs. This type of material was shown to possess promising oxide scale properties in respect to growth rate in both anode and cathode atmospheres, oxide adherence and electrical resistance. Besides, these steels have a more suitable CTE than the commercial alloys 1.4247 or 446 (Fe25CrMnSi). Furthermore, the (Mn,Cr)3O4 spinel-forming steels showed lower chromium evaporation rates than pure chromia-forming alloys. Further studies will concentrate on an extensive characterization and fine-tuning of the materials to reach the adequate combination of properties required for the interconnect in SOFC applications, especially long term oxidation resistance and formation of volatile species in the cathode gas. Continuation of electrical resistance measurements will be necessary, to gain a better understanding of the correlation between resistance and oxide composition.
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Electrochemical Society Proceedings Volume 2001-16 815
Figure 1. Summary of weight change data and scale morphologies on the model alloys after 1000 h exposure at 800°C in air.

Figure 2. a) Electrical contact resistance of selected model alloys at 800°C in air compared with ceramic interconnect of 5mm thickness, b) microstructure of the scale formed on model alloy Fe25CrMn (Ti,La) after 600 h conductivity testing in air.
Figure 3. Comparison between oxidation in air and Ar/H₂-H₂O at 800°C for 1000h.
Figure 4. Cross-sections of various alloys after 1000 h oxidation in air (a-c) and in Ar-H₂-H₂O (d-f) at 800°C.

Figure 5. XRD analysis after 1000 h oxidation in air and in Ar/H₂-H₂O of (a) FeCrMn (Ti,La) and (b) FeCrMn at 800°C.
Figure 6. Thermal expansion coefficient of SOFC components: (○) steel 1.4247, (□) model steel Fe25CrMn (Ti,La), (◇) commercial alloy 446, (△) model steel FeCrMn.