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HIGH TEMPERATURE OXIDATION OF Fe22Cr-ALLOY

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Abstract

The isothermal and constant heating rate oxidation behaviour of the alloy $Fe_{78}Cr_{22}$ was examined in air with 1% H_2O and in 7% H_2/93% Ar with 1% or 12% H_2O. The measurements were performed in the temperature range 700–1300°C. The effect of surface treatment prior to oxidation was examined. A Cr_2O_3 scale developed slowly up to 900°C. At 1100°C a catastrophic oxidation was observed after heat treatment for 70 h in air with 1% H_2O and in 7% H_2/93% Ar with 12% H_2O. The scale developed in these cases consisted of iron rich oxides such as Fe_2O_3 or $FeCr_2O_4$, in contrast to the more protective Cr_2O_3 scale seen under other test conditions. Possible causes for the catastrophic oxidation are discussed.

Keywords: catastrophic oxidation, oxide scales, surface morphology

Introduction

The interconnectors in a solid oxide fuel cell stack (SOFC) provide the electrical contact between single cells and separates the fuel on the anode side from the oxidant on the cathode side during operation. Doped lanthanum chromites or relatively expensive high-Cr alloy composites have previously been used as interconnector materials [1]. However, lowering of the operational temperature, from around 1000°C to 750–850°C, opens the possibility of using cheaper alloys. The alloy must satisfy several requirements (e.g. [2]). Chromia forming alloys are usually considered as the best metallic interconnector materials. This is due to a rather slow growth rate and a proper electric conductivity of the oxide scale [3]. The $Fe_{78}Cr_{22}$ alloy has earlier been identified as a promising material for the use as interconnector [1]. In the present work, the oxidation behaviour of this alloy has been investigated under conditions that resemble SOFC operational conditions.

Experimental

The 200 μm thick $Fe_{78}Cr_{22}$ foil was cut into pieces of 25×15 mm^2. A hole (∅=4 mm) was drilled in each of the pieces for suspension. The chemical composition for the alloy is given in Table 1.

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Table 1 Chemical composition of the $Fe_{78}Cr_{22}$ alloy

Element	C	Si	Mn	Cr	Ni	V	Other	Fe
Mass/%	0.02	0.31	0.27	21.6	0.19	0.03	<0.1	bal

The final surface treatment of the specimens prior to oxidation tests was either HF etching or grinding using 1000 grid SiC paper. The final surface preparation and the test conditions are given in Table 2.

Table 2 Surface preparation and test conditions for the samples

Sample	Dwell time/ heating rate	Gas	Surface preparation	Temperature/ °C	pH_2O/ atm
S1	70 h	air	1000 SiC	700	0.012
S2	70 h	air	1000 SiC	900	0.012
S3	70 h	air	1000 SiC	1100	0.012
S4	70 h	7% H_2/93% Ar	1000 SiC	700	0.012
S5	70 h	7% H_2/93% Ar	1000 SiC	900	0.012
S6	70 h	7% H_2/93% Ar	1000 SiC	1100	0.012
S7	70 h	7% H_2/93% Ar	HF	700	0.122
S8	70 h	7% H_2/93% Ar	HF	900	0.122
S9	70 h	7% H_2/93% Ar	HF	1100	0.122
S10	2°C min^{-1}	air	HF	RT→1300	0.012
S11	2°C min^{-1}	7% H_2/93% Ar	HF	RT→1300	0.012
S12	2°C min^{-1}	air	1000 SiC	RT→1300	0.012
S13	2°C min^{-1}	7% H_2/93% Ar	1000 SiC	RT→1300	0.012

Thermogravimetric analyses were performed with a Netzsch STA439 equipment in air or in 7% H_2/93% Ar in the temperature range of 700–1300°C. The atmospheres were humidified by passing the gas through water at 10°C. This corresponds to a pH_2O of 0.012 atm at room temperature. The resulting pO_2 for the 7% H_2/93% Ar gas was in the range $4\cdot10^{-23}$ to $7\cdot10^{-13}$ atm in the temperature range of 700–1300°C. The TG analyses were not corrected for buoyancy. Temperature scans were made in each atmosphere from room temperature to 1300°C using heating and cooling rates of +2 and –5°C min^{-1}, respectively. Isothermal experiments were performed at 700, 900 and 1100°C for 70 h.

In addition, isothermal experiments were performed in a furnace at 700, 900 and 1100°C for 70 h in 7% H_2/93% Ar humidified with water at 50°C. This corresponds to a pH_2O of 0.122 atm at room temperature and a pO_2 in the range of $6\cdot10^{-21}$ to $3\cdot10^{-13}$ atm in the temperature range of 700–1100°C.

The surface morphology and chemical analyses of the scales were subsequently analysed using a scanning electron microscope (SEM) equipped with an energy-dispersive X-ray analyser (EDX). X-ray diffraction (XRD) studies of the scales were made at room temperature using CuK_{α} radiation.

Table 3 Scale composition determined by XRD. Isothermal heat treatment at 70 h (see Table 2 for test conditions)

Sample	Scale composition
S1	Cr_2O_3
S2	Cr_2O_3,$FeCr_2O_4$
S3	Fe_2O_3
S4	Cr_2O_3
S5	Cr_2O_3, $FeCr_2O_4$
S6	Cr_2O_3, $FeCr_2O_4$
S7	Cr_2O_3
S8	Cr_2O_3, $FeCr_2O_4$
S9	Fe_2O_3, Cr_2O_3, $FeCr_2O_4$

Results and discussion

Constant heating rate

Figure 1 shows the mass gain as a function of temperature for sample S9-S13. The initial part (up to approx. 900°C) of the oxidation proceeds slowly. The surface-grinded alloys gain mass faster than surface-etched alloys, disregarding the atmosphere. The grinded alloys will have mechanically created defects at the polished surface and hence a larger effective surface area than the etched alloys. Also, the higher surface energy for the grinded surfaces could result in absorption of more wa-

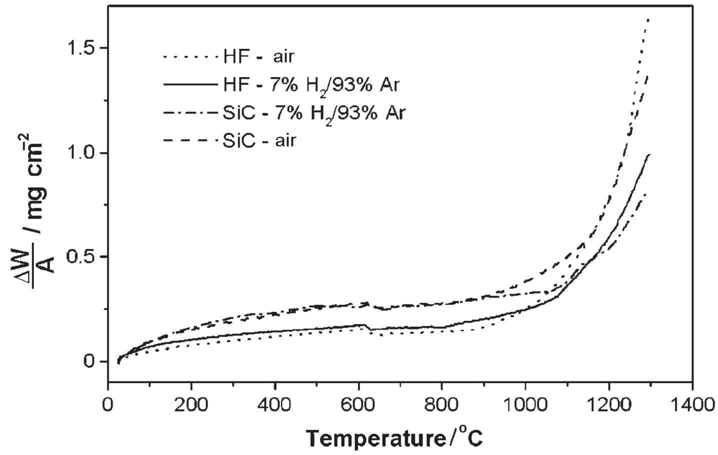

Fig. 1 The mass gain as a function of temperature for sample S9–S13

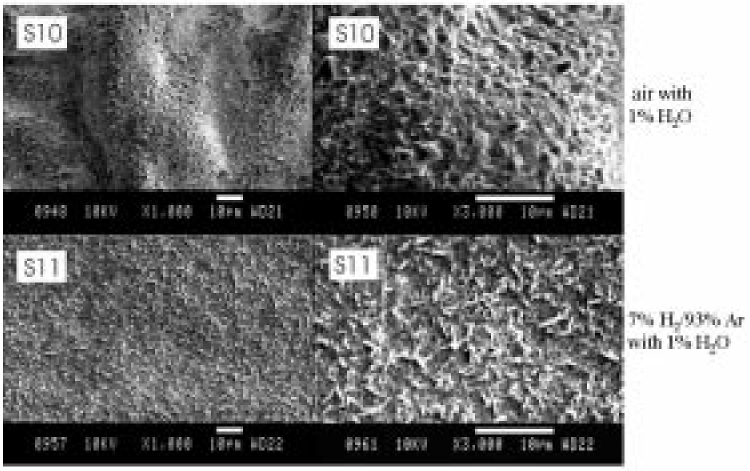

Fig. 2 SEM micrographs of the surface of sample S10 (top) and S11 (bottom). The images are shown in different magnifications. Sample S10 and S11 have been heated from room temperature to 1300°C at 2°C min^{-1}

ter or oxygen at low temperature (<500°C) than the etched alloy. However, further experiments are necessary to elucidate this difference.

In Fig. 1 the oxidation rate is seen to increase rapidly above approx. 900°C. The mass gain does not seem to show any particular correlation to the surface preparation at temperatures above 900°C. It should be noted that the scales grown in air gain more mass than the scales grown in 7% H_2/93% Ar at temperatures above 1100°C.

Figure 2 shows micrographs of the surface of sample S10 and S11. Samples heat-treated in air shows a buckling scale, while the sample oxidised in 7% H_2/93% Ar shows whisker formation. The surface grains are 1–2 μm when grown in air and ≈0.2 μm when grown in 7% H_2/93% Ar. This has also been observed by Linderoth and Larsen [4] for Cr-rich alloys. This difference in grain size might have an influence on the protectiveness of the scale. The very different surface appearances show that the growth mechanism of the scales in the two atmospheres proceeds differently. The oxygen partial pressure seems to have an influence on the morphology of the scale. Further investigations are necessary to elucidate this behaviour. Cross section of the samples S10 and S11 are shown in Fig. 3.

The scale of the alloy treated in 7% H_2/93% Ar (S11) has a uniform thickness of 5–6 μm, while the scale grown in air (S10) shows cavities in good accordance with the buckling of the scale shown in Fig. 2. Assuming the scale to be Cr_2O_3 the mass gain at 1300°C shown in Fig. 1 corresponds to an average scale thickness of approx. 6 and 10 μm for the scale grown in air and 7% H_2/93% Ar, respectively. This in good accordance with the average scale thickness shown in Fig. 3. EDX and XRD verified that the scale consists of Cr_2O_3.

Dark spots are clearly seen beneath the scale. These spots were identified as Si-oxide by EDX-analyses. However, it was not possible to identify any crystalline

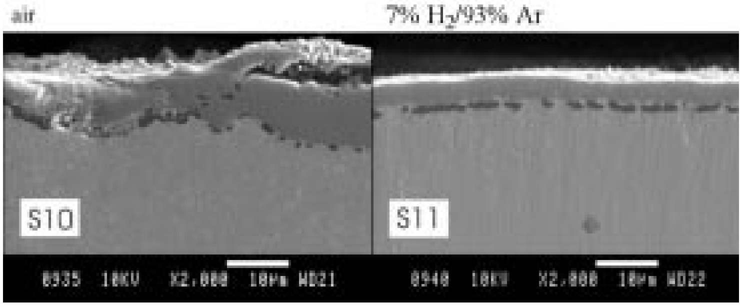

Fig. 3 SEM micrographs of the cross section of sample S10 and S11. Sample S10 and S11 have been heated from room temperature to 1300°C at 2°C min^{-1}

phase of SiO_2 by XRD. The Si-oxide has formed a discontinuous layer beneath the Cr-oxide scale. The Si-oxide layer is clearly separated from the Cr-oxide scale by a metal. A similar behaviour has been reported for Ni-Cr alloys by Saito and Maruyama, but an explanation was not given [5]. In the following we propose the cause of this phenomenon. A Cr scale is initially formed due to the difference in oxygen affinity between Cr and Fe. The present Si will also oxidise, but given the relatively low Si concentration (Table 1) the initial formed Si-oxide cannot be determined in the scale. During the prolonged heat treatment Si diffuses by random walk to the interface between the metal and the Cr-scale. Since Si has a larger oxygen affinity than Cr, a redox reaction that results in the formation of Si-oxide and elemental Cr takes place. This process can explain the formation of the Si-oxide layer beneath the Cr-oxide scale, separated by a thin layer of metal.

The amount of Si in the alloy is 0.31 mass% (Table 1). If all Si would reach the surface after the 70 h of oxidation, and had formed a dense layer, the thickness should be about 1.8 μm. From Fig. 3, it may be estimated that less than 50% of the Si has reached the surface at this stage of oxidation.

Isothermal heating

The mass gain for the isothermal oxidation at 900 and 1100°C in two different atmospheres are shown in Fig. 4. The heat treatments were also carried out at 700°C, but the alloys only showed little mass gain at that temperature. The total mass gain for all the alloys after 70 h of oxidation is shown in Fig. 5.

Figure 6 shows micrographs of the morphology of the scales. The scale of sample S9 was thin at the middle of the alloy and thick near the edges. The image in Fig. 6 shows the thin central part. The microstructure of sample S2 and S5 show the same trends as were seen in Fig. 2, i.e. surface grains grown in air where larger than grains grown in 7% H_2/93% Ar. The scale grown in air at 1100°C had large grains, which were identified as α-Fe_2O_3 by XRD. The grain size at the surface of the scales grown in 7% H_2/93% Ar with 1% H_2O or 12% H_2O are similar. This indicates that the water

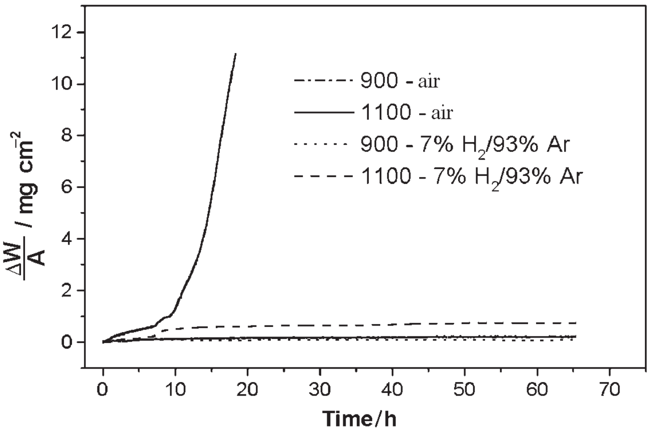

Fig. 4 Mass gain of the alloy at isothermal oxidation at 900°C and 1100°C in air or 7% H_2/93% Ar, both with 1% H_2O

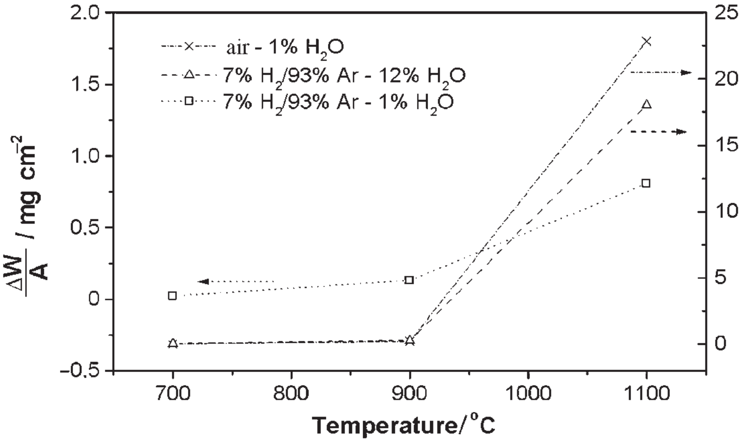

Fig. 5 The mass gain for the Fe22Cr alloy is shown after isothermal oxidation at 700, 900 and 1100°C in 70 h. The alloys were heat treated in different atmospheres

partial pressure in a low pO_2 atmosphere does not have a dramatic influence on the morphology of the scale.

It should also be noted (Figs 1 and 5) that the scales grown in air gain mass faster than the scales grown in 7% H_2/93% Ar. Thus, the oxygen partial pressure seems to have an effect on the oxidation kinetics. However, Brylewski *et al.* [6] have earlier reported that the oxidation kinetics for an Fe16Cr alloy is independent of the oxygen partial pressure. Further investigations are necessary to explain the differences.

In contrast to the sample oxidised in 7% H_2/93% Ar with 1% H_2O the alloy oxidised in air with 1% H_2O at 1100°C revealed a catastrophic oxidation after ≈10 h.

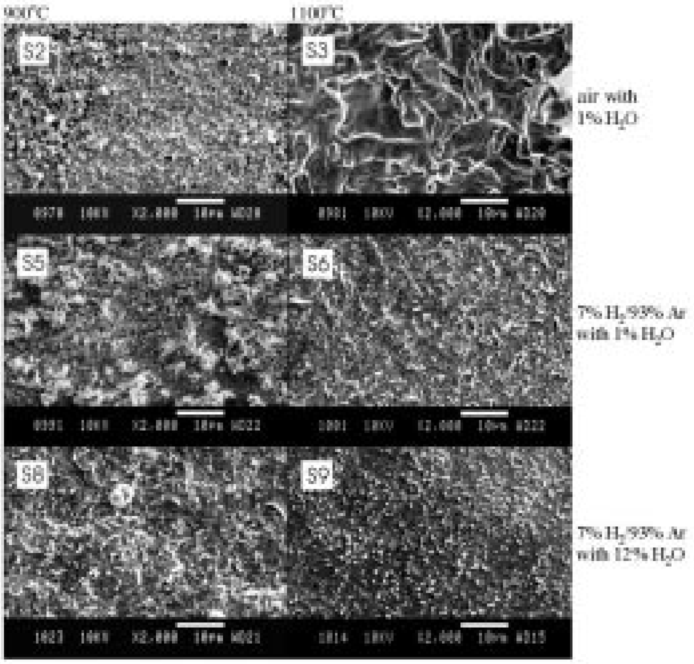

Fig. 6 SEM micrographs of the scale after isothermal oxidation in 70 h at 900°C (left) or 1100°C (right) in different atmospheres

Cracks or pores in the scale may initiate the catastrophic oxidation of the alloy. Such cracks could be a result of mechanical stress that builds up in the scale due to differences in the growth rate or growth direction within the oxide scale [7]. This can then be followed by penetration of oxygen to the scale/alloy interface. Given a Cr depletion at the alloy surface iron oxide will start to form and thereby provide a significant increase in the reaction rate [8, 9].

In the case of a dense crack-free scale the initial preferential oxidation of chromium, causes a Cr depletion at the surface of the alloy. If the diffusion rate of chromium is low or the initial concentration in the alloy is small, the chromium concentration might drop to a critical value, such that an oxidation to the spinel $FeCr_2O_4$ or an iron oxide becomes thermodynamically possible [10]. The iron oxidises very fast and might create cracks in the scale. This will, in turn, create a catastrophic oxidation of the alloy. Experiments are ongoing to explore this further.

The alloy oxidised in 7% H_2/93% Ar with 12% H_2O also showed catastrophic oxidation behaviour at 1100°C. This is in contrast to the case of oxidation in 7% H_2/93% Ar with 1% H_2O. After oxidation, the surface consisted of a thin scale at the middle of the alloy and a thick scale at the edges. This indicates that the catastrophic oxidation was initiated at the edges of the alloy. This behaviour has also been observed by Shen *et al.* [9]. The different oxidation behaviour in the two 7% H_2/93% Ar-gasses indicates that increased partial pressure of water has a negative effect on the oxidation resistance of the alloy [11, 12]. It is well documented that presence of water has a negative effect on the rate of oxidation. However, the reasons are not understood [11]. It has been proposed that protons from the water dissolve in the oxides and thereby change the defect chemistry of the oxide scale. According to this, the oxygen transport will decrease, while there will be an increased transport of metal across the scale [11, 12]. This will lead to an increased oxidation at the gas/scale interface. Also, it might in turn create voids at the alloy/scale interface and subsequently lead to cracks in the scale. It has earlier been observed that the content of water vapour in oxygen has a direct effect on the stage of the catastrophic oxidation by Shen *et al.* [9]. They found that the catastrophic oxidation started earlier for Fe–Cr-alloys with increasing water content in oxygen.

The scale composition after heat treatment was analysed by XRD and EDX. The protective scales consisted of Cr_2O_3, some with a minor amount of $FeCr_2O_4$. The non-protective scale for the alloy oxidised in air consisted of large crystallites of Fe_2O_3. The non-protective scale on the alloy oxidised in 7% H_2/93% Ar with 12% of water vapour consisted of Cr_2O_3 with a minor amount of $FeCr_2O_4$ at the thin scale at the middle of the alloy, and Fe_2O_3 at the thick scale near the edges. The catastrophic oxidation was initiated by the oxidation of iron oxides as explained earlier.

Conclusions

The oxidation behaviour of the alloy $Fe_{78}Cr_{22}$ was examined in various atmospheres. The oxidation kinetics does not show a correlation to the surface preparation above 900°C. Scales grown in air consisted of large grains and gain mass fast compared to scales grown in 7% H_2/93% Ar. At 1100°C catastrophic oxidation occurs for the sample oxidised in air with 1% H_2O. This was not the case when oxidised in 7% H_2/93% Ar with 1% H_2O. However, when increasing the water content to 12% in 7% H_2/93% Ar catastrophic oxidation was seen. Si-oxide was seen at the scale/alloy interface. This is caused by the high affinity of Si towards oxygen. A mechanism is put forward. Further investigations are necessary to elucidate the mechanism of the oxidation behaviour as a function of temperature and atmosphere.

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