

Short communication

Evaluation of ferritic steels for use as interconnects and porous metal supports in IT-SOFCs

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Abstract

As a way of reducing the production costs of stacks by replacing ceramic components with metal components with a similar thermal expansion coefficient (TEC), today, much of the research work has focused on SOFCs operating at temperatures of under 800 °C. Some semi-commercial ferritic stainless steels (FSS) satisfy this TEC. Ikerlan has evaluated samples of two of these. Also, AMETEK stainless steel powders were tested in sintered disks until they were completely densified in order to compare results from dense and porous materials. The first tests performed by Ikerlan were conducted with dense samples and included the oxidation test in air at 800 °C and measurements of contact surface electrical resistance (area specific resistance, ASR), to compare electrochemical techniques (electrochemical impedance spectroscopy, EIS) with the traditional four-wire method and indirect measuring of the resistance through current and voltage measurements. An alloy from the last melt manufactured by the company ThyssenKrupp VDM GmbH performed best. These results did not differ greatly from the previous laboratory results attained during alloy development. Only AMETEK powder metallurgy materials were tested as porous bodies, to compare these with these dense materials, and were found to provide much higher oxidation levels, as might be expected. While dense materials can operate under the working conditions of the SOFC, porous materials still need new alloys.

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1. Introduction

The approach of Ikerlan's SOFC project [1] is similar to those of other research units [2–4], although it has planned a tubular geometry instead of a planar one for the prototype and a different final application in domestic generators that produce HSW and electricity. The basis is an operating temperature of under 800 °C, so that ceramic components, such as the bracket for the electrochemical ceramics and the interconnect, can be replaced with metal components. In view of the fact that Ikerlan plans to use metallic components to

develop solid oxide cells, one of the main aims is to search for the optimum alloys for our system.

There is a great deal of scientific literature dealing with this problem, including a number of reviews [5,6]. The main characteristic that determines the validity or not for using these high temperature metal alloys in IT-SOFCs is the thermal expansion coefficient (TEC), which in turn must be similar to the ceramic materials used ($11 \times 10^{-6} \text{ K}^{-1}$ for YSZ electrolyte between 20 and 1000 °C [7]) in order to prevent the degradation of these cells in the heating and cooling processes. The afore-mentioned metal alloys must also have good corrosion resistance in oxidising (air on the cathode) and reducing atmospheres (methane reformed gas on the anode [8]) up to 800 °C, acceptable electrical conductivity, and thermochemical stability in contact with ceramics (to avoid problems relating to the diffusion of elements between steels and ceramics and the vapourisation of chromium in atmospheres

Abbreviations: ASR, area specific resistance; EIS, electrochemical impedance spectroscopy; FSS, ferritic stainless steel; IT-SOFCs, intermediate temperature solid oxide fuel cells; TEC, thermal expansion coefficient

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with the presence of water vapour) during the lifetime of the IT-SOFC.

Some ferritic stainless steels (FSS) have a thermal expansion coefficient compatible with the YSZ [9]. Previous studies have measured acceptable properties with chromium contents of around 20%, predicting a better electrical conductivity with 22% of chromium [7]. Once that TEC has been obtained, mainly through the chromium contents, another series of elements are added to obtain a greater resistance to oxidation and higher electrical conductivity [5,6].

The limited life due to oxidation is primarily governed by the reserve of scale-forming alloying elements, in our case, mainly Cr, rather than by their absolute concentrations in steel. Because of the large parabolic oxidation rate/diffusion coefficient ratio in FSS at intermediate temperatures, a steep slope of the depletion profile beneath the oxide scale is expected to occur [10]. Parabolic rate constants should be less than 10^{-14} g² cm⁻⁴ s and preferably below 10^{-15} g² cm⁻⁴ s [11].

The area specific resistance (ASR) of an oxidised metal is mainly dominated by that of the oxide layer. In the case of FSSs, an Arrhenius behaviour can be derived from ASR curves which implies a process activated by temperature (i.e., electron–hole promotion to the valence band, diffusion of ionic defects. . .). Also, a parabolic oxide growth can be derived from the ASR data [4]. The increase in oxidation resistance and the decrease in the ASR by adding small amounts of yttria demonstrate that the relationship between the oxidation rate and ASR is high (even a mathematical relationship can be derived). Other dopants, such as NiO, can improve the electric conductivity of the chromia scale, which also demonstrates its extrinsic behaviour [12]. The target of the research in oxidation and ASR for interconnects is that, after thousands of hours of oxidation, the surface resistivity should not exceed 50 mΩ cm² [9], i.e., less than 5% of power losses, depending on the power density.

Ikerlan has assessed a number of commercial alloys, as well as almost fully densified 30% chromium containing FSS powder. The aim was to compare oxidation and ASR properties from well-known dense materials with those from porous ones.

2. Experimental

An evaluation was made of two commercial metal alloys with a chromium content of a little more than 20%, present in the literature and used by some research groups as interconnects [5]: two samples of Crofer22 APU, made by the company ThyssenKrupp VDM GmbH, from different melts, and another sample, ZMG 232 made by Hitachi Metals. Three samples of FeCr (70:30) (AMETEK), powder metallurgy material currently used by Ikerlan, were also sintered to more than 90% of theoretical density.

For the oxidation test, three 38 mm diameter disks of each alloy (the same size as the porous metallic supports), were

tested. The disks were prepared as follows: polishing using 1200 grit SiC paper, degreasing, washing in a ultrasonic cleaner and weighing. The samples were then placed in a muffle furnace at 800 °C, in air with uncontrolled humidity, suspended by platinum wires. The first disk was removed from the furnace after 100 h, a second one after 200 and the last one after 1000 h. Each was weighed after being removed from the furnace.

The same test was performed with the FeCr (70:30), but with porous disks identical to the ones used later as substrates of the ceramic electrochemical part [1]; three disks with an average particle size of 45 μm (–140/+325 mesh) and porosities of around 50%, and another three with an average particle size of 32 μm (–325/+15 mesh) and porosities of 30%.

ASR measurements were made comparing electrochemical impedance spectroscopy (EIS) electrochemical techniques with the traditional four-wire techniques and indirect measuring of the resistance by supplying a current (in the range of 4–1000 mA cm⁻²) and measuring the voltage. The sample was prepared by covering with 1 cm² Pt paste and using a Pt mesh as a current collector [12]. Once the sample had been placed in an open furnace and as the temperature increased, it was connected to the Solartron 1286 electrochemical interface (used with a Solartron 1260 impedance/gain-phase analyser) for the EIS test, or to the HP 34410 A multimeter for the four-wire method, or a current was applied to it and the voltage was measured in order to calculate the resistance.

The linear behaviour of the ASR as a function of the applied current was observed at constant temperature, so, in order to obtain a more accurate result, the test was carried out at a high current density.

No ASR measurement was made of the porous samples, as they were too oxidized.

3. Results

Data from the oxidation test of non-porous samples are shown in Fig. 1. Comparable results to those described in the publications of other work units were obtained for Crofer22

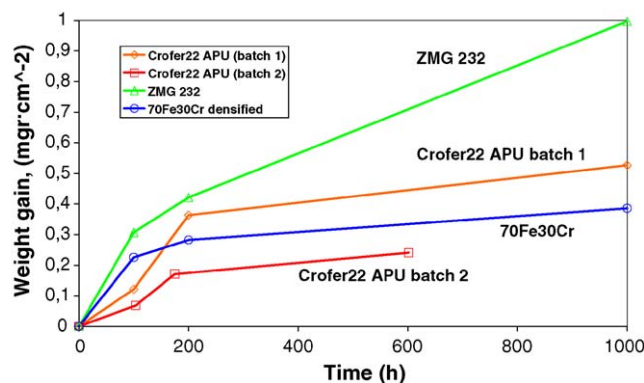


Fig. 1. Mass gain of non-porous samples in air at 800 °C.

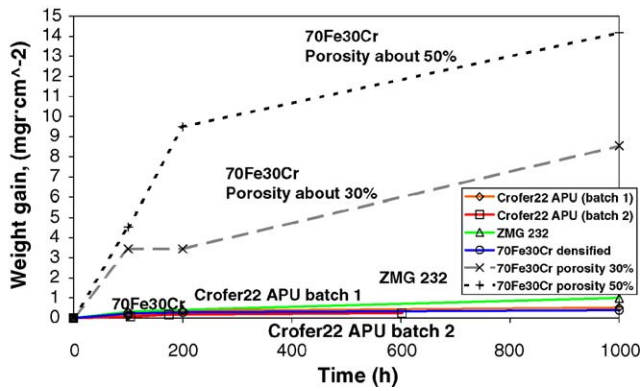


Fig. 2. Mass gain of porous and non-porous samples in air at 800 °C.

APU from the first melt [10]. The FeCr sample (70:30), densified by powder metallurgy to the theoretical density, showed good performance in an oxidising atmosphere as it had high chromium content. The best results, however, were obtained with Crofer22 APU from the last melt, in spite of the fact that it had a lower chromium content.

Fig. 2 shows all the data of the oxidation test together, of porous and non-porous samples. By oxidising porous samples of the same steel FeCr (70:30) under the same conditions, the most oxidised sample is the most porous, as might be expected.

For chromium oxide layers that follow Wagner’s theory (the mass gain follows a parabolic curve) it is more appropriate to calculate the instantaneous parabolic constant k_p , as in fact it is not a constant [5]. The first stages of oxide scale formation are better described in this way. In our case, the mean k_p was calculated (Table 1) as the samples were weighed only after 100, 200 and 1000 h to measure the ASR with these oxidation times.

By comparing different ASR measurement techniques, EIS was the technique that gave the worst results for high resistances because of the difficulty in controlling low temperatures (the precision in ASR measurements by EIS is good for the temperature range, but it is difficult to maintain the temperature). On the other hand, on measuring few mΩ s, the precision of the multimeter used is more or less of the same magnitude, so it is impossible to reach an accurate result.

The indirect method was chosen because ASR can be measured during heating and cooling accurately in a quasi-continuous way (EIS is too sensitive to temperature change).

Table 1
Mean k_p parabolic constants

	Mean k_p ($\times 10^{-13}$ g ² cm ⁻⁴ s ⁻¹)
ZMG 232	2.7
Crofer22 APU (batch 1)	0.8
Crofer22 APU (batch 2)	0.28
70Fe30Cr densified	0.57
70Fe30Cr 140/325	650
70Fe30Cr 325/15	206

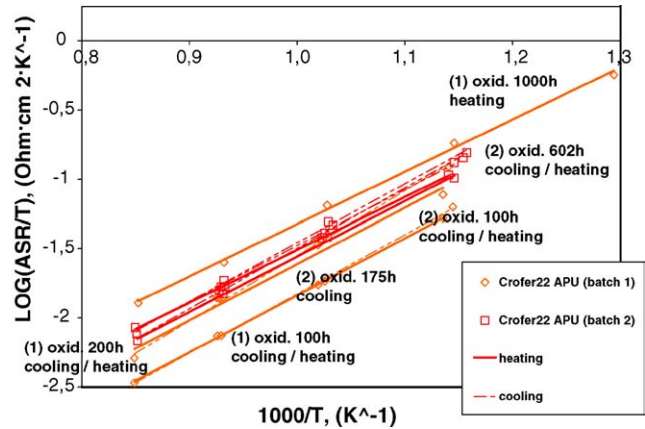


Fig. 3. ASR dependence on temperature for Crofer22 APU samples oxidised in air at 800 °C for different times.

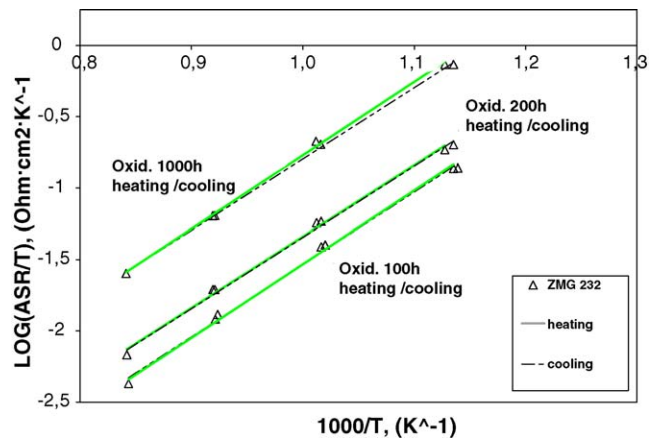


Fig. 4. ASR dependence on temperature for ZMG232 samples oxidised in air at 800 °C for different times.

Reproducible results were obtained for Crofer22 APU, ZMG232 and FeCr (70:30) during the heating and cooling processes.

Figs. 3–5 shows dependence of ASR on temperature for Crofer22 APU, ZMG232 and FeCr (70:30) samples oxidised

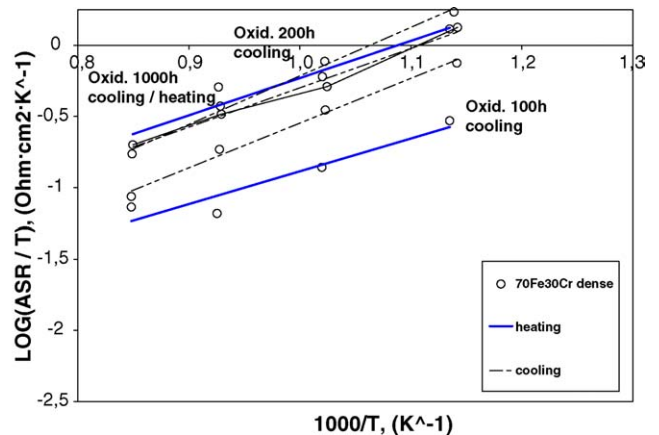


Fig. 5. ASR dependence on temperature for FeCr (70:30) samples oxidised in air at 800 °C for different times.

Table 2
Activation energies for ASR in eV

Oxidation time (h)		Activation energies (eV)
ZMG 232		
100	Heating	1.02
	Cooling	1.01
200	Heating	1.02
	Cooling	0.99
1000	Heating	0.99
	Cooling	0.99
Crofer22 APU (batch 1)		
100	Heating	0.82
	Cooling	0.85
200	Heating	0.8
	Cooling	0.93
1000	Heating	0.75
	Cooling	
Crofer22 APU (batch 2)		
100	Heating	0.8
	Cooling	0.86
175	Heating	
	Cooling	0.84
602	Heating	0.76
	Cooling	0.8
70Fe30Cr densified		
100	Heating	0.46
	Cooling	0.62
200	Heating	
	Cooling	0.68
1000	Heating	0.52
	Cooling	0.55

in air at 800 °C for different times. The activation energy (E_a) for these processes was calculated (Table 2). The highest E_a s were for ZMG232.

Fig. 6 describes the dependence of extrapolated ASRs at 800 °C in air on the oxidation time. The measured ASR for

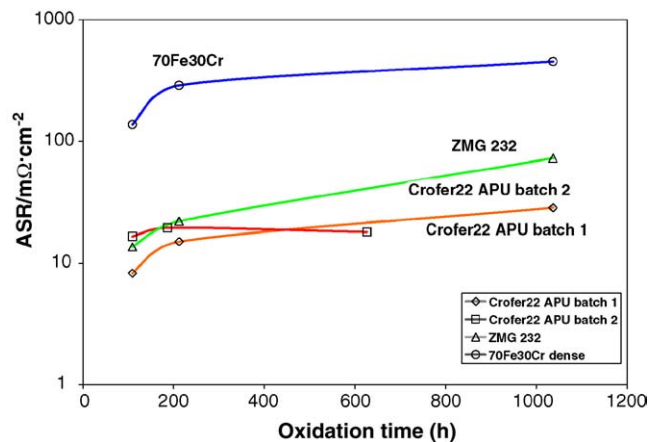


Fig. 6. Extrapolated ASRs at 800 °C in air. Its dependence on oxidation time in air at 800 °C for Crofer22 APU, ZMG232 and FeCr (70:30) samples.

Crofer22 APU is slightly higher than that found in the literature, while for ZMG232, this is of the same magnitude [13]. The best ASR was also for Crofer22 APU from the second melt.

4. Conclusions

Despite its lower Cr content, Crofer22 APU performed better than the AMETEK sintered disk because of the different microalloying [5,6]. The difference between the samples from batch 1 and batch 2 were mainly based on improvements in the manufacturing processes at ThyssenKrupp VDM. If we compare these with the laboratory tests (JS-3), lower oxidation resistances for this composition were obtained because of manufacturing related impurities [5].

The different behaviour between JS-3 and ZMG 232 is described in Ref. [14], and is due to a SiO₂ layer formed between the chromia and the ZMG 232 metal substrate under oxidation test in air.

Calculated activation energies were lower than that of the single crystal Cr₂O₃, which indicate an extrinsic behaviour, an electrical conductivity dominated by impurities in the chromia scale [12]. In the case of FeCr (70:30), a pure chromia scale is supposed to be formed, so activation energies higher than 0.9 eV were expected. However, lower values were obtained. This may be due to some kind of impurity (problems with Si were detected during testing some cells). Although the measurement at 900 °C lasted less than 10 min, an increase in ASR was observed. This is because at that high temperature the sample oxidises very quickly. This is the reason why activation energies differ during heating and cooling.

ZMG 232 and Crofer22 APU have lower ASR than FeCr (70:30) because of a number of specific additions.

The ASR curve describes a parabolic behaviour, which agrees with the parabolic oxide growth. The fact that, for oxide scales with the same composition, the best performing sample against oxidation also had the lowest ASR, confirms the close relationship between oxidation resistance and ASR.

As described in previous literature, dense materials can operate under the working conditions of the SOFC, although working preferably below 800 °C. Porous materials still need new alloys.

5. Future work

Oxidation tests and ASR measurements of more different materials are planned for the future. An attempt will be made to define the most useful parameter for volume to surface ratio for porous bodies, in order to calculate lifetimes in high temperature corrosion. The objective is to find the best performing commercial material for use as a porous substrate.

The next step will be to define a method to measure ASR in porous bodies and, moreover, to look for a relationship between ASR and porosity in order to extrapolate the properties of a porous material from the properties of a dense one.

Microscopy will be used to establish the composition of the characteristic oxide layer, as well as to determine the diffusion of elements after testing different FSS in contact with anode ceramics in reducing atmospheres.

To enable these projects to be carried out, a collaboration project with the company Ames and the University of Carlos III has been submitted to the PETRI programme in Spain.

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