APPLICATION OF FERRITIC STEELS AS SOFC INTERCONNECTS UNDER REAL CONDITIONS

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ABSTRACT
On the way to commercialisation of SOFC technology, low cost components are crucial and in particular cells and interconnects play a key role in the system price. For interconnects, ferritic alloys potentially provide a cheaper solution than chromium-based components, due to better formability and lower procurement cost. However, oxidation has to be investigated closely, especially at temperatures as high as 950°C, as these alloys tend to form low conductive oxide layers with a risk of delamination. Electrochemical tests under realistic conditions and contact resistivity measurements were performed during 2000 hours of operation. These tests showed that, if coated, the ferritic steels under consideration are indeed serious candidates for interconnects.

INTRODUCTION
The SOFC system developed by Sulzer Hexis is based on a planar, electrolyte supported concept operating at 950°C. The elevated temperature has advantages like high ionic electrolyte conductivity and allows a proper combustion of surplus fuel gas for heat and power cogeneration. On the other hand, affordable materials meeting the long term requirements of the stack, particularly for interconnects, are harder to obtain. The criteria for the selection of an interconnect material are well known:

- Thermal expansion coefficient (CTE) close to zirconia-supported cells ($\alpha_{RT-1000^\circ C}=10.65$ ppm/K) to avoid cracking in the stack during thermal cycling.
- Good electrical conductivity and long term stability of the bulk material and its oxide scales at elevated temperatures over up to 40,000 hours.
- Good adhesion of the oxide scales even after thermal cycles.
- Gas impermeability to separate the fuel from the air atmosphere.
- Low porosity within the bulk material to avoid warping due to internal oxide growth.
- Manufacturing possibilities of forming channels and dimples into metal sheets to achieve a certain gas flow and appropriate contact to the cell.
- Low cost of raw materials and machining, as considerable number of interconnects are used within a stack.
- Preferably good thermal conductivity to improve temperature distribution over the entire area of the cell.
- Alloys susceptible to chromium evaporation should be compatible with a protective coating.
Ceramic interconnects are successfully used in certain applications (1), partially for their high temperature stability and their excellent expansion match with the cells. However, metallic interconnects could be favourable in terms of price, reliability and electrical conductivity. Therefore Sulzer Hexis has always been using the Plansee Cr5Fe1Y2O3 alloy, which can be supplied as a dense sheet made by hot isostatic pressing (HIP) and later be machined or as near-net-shape pressed, and sintered parts made by powder metallurgy (2). In parallel, ferritic steels are tested as an alternative solution. As a number of publications have already shown that none of the traditional commercial alloys like 1.4742, 1.4749 or 1.4509 would hold up to the requirements (3, 4, 5), the interest was focused on new compositions that were especially developed for SOFCs.

The tests discussed below intended to simulate the real environment of Sulzer Hexis stacks, so electrochemical testing was performed with coated interconnects at 950°C, including thermal and redox cycles. Whenever possible, metal sheets made with a mass-production process were used. As a standard design, the current powder metallurgy interconnect design was chosen. The manufacturing of the ferritic interconnects was based on sheet material. After adaptation of the technology for interconnect’s specific needs, this process can now be qualified and up-scaled. As it is known that chromium evaporation is detrimental to the cathode, a protective coating was applied on the cathode side of the interconnects which at the same time slowed the oxidation growth of the alloys. The thermal coating process was equally a mass-production process, which is currently used for the Sulzer Hexis standard interconnects. Other conditions like the sulphur-containing natural gas, the temperature gradients etc. were chosen as they are encountered in field systems.

EXPERIMENTAL

Electrochemical Testing

All electrochemical measurements were made in Sulzer Hexis 5-cells stack test rigs at 950°C. The stacks consisted of round cells of 100 cm² area, based on 3YSZ electrolytes and currently used electrodes. The stacking was done in the usual way including contact slurries. The interconnects were coated with a protective layer, which was applied by high velocity oxygen-fuel (HVOF) spraying. All interconnects are made with the current standard Hexis design.

Process fuel was natural gas with the usual sulphur content, it was reformed by catalytic partial oxidation (CPO). The tests were performed by imposing a constant current and the voltage of every cell was individually measured through connected platinum wires. During redox cycles the gas was turned off for at least 4 hours and then turned back on while temperature was kept constant, whereas during a thermal cycle the temperature was lowered to room temperature. During the thermal cycles, the cells were exposed to air.

SEM Characterisation

Metallographic specimens showing the cross-sections of the interconnects after electrochemical testing were ground and polished. Pictures were taken with a JEOL JSM-848IC scanning electron microscope.
Contact Resistivity

Contact resistivity was measured in a laboratory furnace at 950°C in air by a four point method. Square samples (19 mm x 19 mm) were cut out of coated interconnectors, each sample containing 36 dimples. Only the real contact area was counted for calculating the ASR values. A contact slurry was applied before placing a cathode plate (with a platinum mesh fixed with Pt-paste) on top, see figure 1. The resistance of the cathode plate was subtracted to calculate the contact resistance. The whole assembly was weighed down with a small Al₂O₃ block. Resistance was automatically measured every hour.

Figure 1. Set-up for contact resistivity measurements.

RESULTS AND DISCUSSION

Multiple electrochemical tests were conducted according to figure 2. Tests were conducted under identical conditions (cell batch, gas input, gas quality, interconnector design etc.). Differences are pointed out in table 1. Plansee Cr₃Fe₁Y₂O₃ interconnects were used as a benchmark.

Figure 2. Test programme run on different interconnects. Cell voltages and current are shown for steel 1. Temperature was 950°C and gas input was 260 W. Thermo-and redox cycles are indicated.
Table 1. Differences in the electrochemical testing programmes.

| alloy         | thermal cycles | redox cycles | duration (hours) | imposed current (A) |
|--------------|----------------|--------------|------------------|---------------------|
| Cr5Fe1Y2O3   | 3              | 1            | 4000             | 20                  |
| Steel 1      | 3              | 2            | 2200             | 20/25               |
| Steel 2      | 3              | 2            | 2200             | 15                  |
| Steel 3      | 3              | 2            | 2200             | 20/25               |

Starting ASR values and degradations of different alloys are compared in figure 3. At the beginning of the tests, all ASR values lie between 1.12 mΩcm² and 1.27 mΩcm². Under constant operation conditions, the degradation of the power output lies between 0.05%/1000 hrs and 0.47%/1000 hrs. If redox and thermal cycles are included, the degradation of the ASR values was between 5%/1000 hrs and 14%/1000 hrs. Values including cycles are subject to large scattering, which is partially due to the influence of the cells. Exceptionally bad cells are not taken into account (e.g. cell 1 in figure 2). Big differences in degradation were encountered whether cycles were included or not into the calculations, which stresses the influence of cycles on the performance.

![Figure 3. Starting ASR values and degradation of stacks. Three ferritic steel stacks are compared to a stack with chromium standard interconnects.](image)

Even though electrochemical testing is a good method to test interconnects under realistic conditions, the results are greatly influenced by the cells, and therefore drawing conclusions over the interconnects has to be done carefully. However, it is obvious (figure 3) that the performance values of ferritic steels are not inferior to the ones for the chromium reference interconnects.

The most important characteristics like CTE, contact resistance over time and machinability have to be tested independently of cells to characterise the interconnect alloys. Concerning machinability, it was found that existing processes can be adapted to suit the needs of ferritic steels.
Thermal expansion coefficients are given by the steel manufacturers and can be easily measured on samples. The concerned materials have CTEs of up to about 13*10^{-6}/K (room temperature to 950°C). It is supposed that these are acceptable values. In fact, even with chromium interconnects, cell cracks are sometimes observed after dismantling the stacks, if they underwent a number of thermal cycles during their lives. Cell cracking does not only depend on the CTE of the interconnects but also on many other parameters like the mechanical stability of the cells, the surface area, the applied force and the temperature gradients. So far, no clear difference has been observed between chromium and ferritic interconnects. However, it is clear that the CTE should be as close as possible to the cells to exclude cell breakage.

To better understand the degradation behaviour of different alloys, contact resistance on the cathode side was measured in a furnace, figure 4. Steel 3 was not tested, as mass-production of this alloy is not possible at present. Steels 4 and 5 did recently appear on the market. Two samples of each composition were tested. Fig. 4 shows the better sample of each alloy.

![Figure 4. Contact resistivity of different ferritic steels and the chromium reference alloy including one thermal cycle.](image)

Four out of five alloys followed parabolic time dependence often observed for oxide growth at high temperatures (6). Their long time behaviour can be extrapolated as shown in table 2, without taking into account any cycles or warping effects due to larger interconnects. The contact resistance of steel 1 grows almost linearly and at 2100 hours overtakes all other samples. In this case, the oxide layer may detach when a certain thickness is reached, which would lead to a significant increase of contact resistance.

| sample              | linear regression, x=vt | ASR decrease for Hexis design |
|---------------------|-------------------------|-------------------------------|
| Cr5Fe1Y2O3          | y (mOhmcm²) = 0.2928x - 0.4053 | 0.48 Ohmcm²                  |
| Steel 2             | y (mOhmcm²) = 0.0149x + 0.3471   | 0.03 Ohmcm²                  |
| Steel 4             | y (mOhmcm²) = 0.1243x - 0.2022   | 0.20 Ohmcm²                  |
| Steel 5             | y (mOhmcm²) = 0.0969x + 0.1521   | 0.16 Ohmcm²                  |

Table 2. General linear regression and extrapolated ASR decrease after 40,000 h for the Sulzer Hexis design.
During the thermal cycle at around 2300 hours, the contact resistance increases additionally. As the samples have not been moved, this is thought to be due to different thermal expansion within the compound or due to some warping behaviour of the interconnects. After the thermal cycles there is an effect of recovery. However, this effect is not as fast as observed in previous tests or as practical concerns for stacks would demand. After 24 hours it was not finished and it has to be seen if the values before the cycle can be reached again.

As the contact resistance measurements are still on-going, SEM pictures made after the electrochemical tests mentioned above were investigated. In this case, delamination was not observed for steel 1, figure 5, but the oxide layer on steel 1 was indeed thicker than the one on steel 2 (picture not shown here). Steel 2 showed a very low contact resistivity in the specific test (fig. 4), but in the cross-section of an interconnect from the electrochemical test a weak area was observed at the interface between the oxide layer and the coating. Steel 1 has also some weak areas (fig. 5), but less pronounced and rather in the protective coating than at the interface.

![SEM picture](image)

**Figure 5.** SEM pictures of steel 1 after 2200 hrs of electrochemical testing including cycles. The interface between oxide and coating is indicated by the black line.

Figure 6 shows three curves shown in fig. 4 and compares them to older data with uncoated alloys. The measurements with the uncoated alloys were conducted at 900°C. It can be seen that the protective coating provides considerable improvement of the oxidation behaviour.

Encouraged by the results from the electrochemical 5-cell tests and the contact resistance measurements, two system stacks were built with ferritic steels and operated with the new Sulzer Hexis system. Figure 7 shows the results with steel 2 interconnects. Due to some unplanned redox cycles at the very beginning of the test, start performance was poor, being around 700 Wdc and 20% electrical efficiency. However, it can be seen that stability without cycling is excellent and that there is no degradation observed over 1800 hours. The second system contained steel 1 interconnects. In this case the start performance was 910W, but degradation was higher than expected. The reason for this is yet to be found.
CONCLUSIONS

- A number of ferritic steels have been tested in 5-cell stacks at 950°C over 2200 hours.
- Starting ASR values as well as degradation values were equivalent of those for stacks with chromium interconnects.
- Contact resistance is clearly decreased by the use of a protective layer.
• The best contact resistivity results allow to extrapolate very encouraging ASR degradation in terms of interconnect oxidation at constant 950°C over 40,000 hours.

• Ferritic steel interconnects can be made out of sheet material through adaptation of existing mass production processes.

• A system stack with ferritic steel interconnect has been running for over 1800 hours at 950°C with no degradation.

FURTHER WORK

• Promising new materials will be included in the 5-cell stack testing as well as in the contact resistivity measurements.

• Contact conductivity tests are still on-going and more thermocycles will be conducted. At the end of the testing, analysis of the sample cross-sections will give additional information about the scales.

• Interconnect warping behaviour will be investigated.

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