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COMPLETE RELAXATION OF RESIDUAL STRESSES DURING REDUCTION OF SOLID OXIDE FUEL CELLS

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Abstract - **To asses the reliability of solid oxide fuel cell (SOFC) stacks during operation, the stress field in the stack must be known. During operation the stress field will depend on time as creep processes relax stresses. This work reports further details on a newly discovered creep phenomenon, *accelerated creep*, taking place during the reduction of the anode. This relaxes stresses at a much higher rate ($\sim \times 10^4$) than creep during operation. The phenomenon has previously been studied by simultaneous loading and reduction. With the recorded high creep rates, the stresses at the time of reduction should reduce significantly over minutes. In this work the stresses are measured in-situ before and after the reduction by use of XRD. The phenomenon of accelerated creep has to be considered both in the production of stacks and in the analysis of the stress field in a stack based on anode supported SOFCs.**

I. INTRODUCTION

Ensuring mechanical stability of SOFC stacks is a key challenge for the commercialization of the technology. To evaluate the reliability of the SOFC stacks during operation, the stress field in the stack must be known. The stresses in a stack evolve over time depending on the operational conditions, external pressures, thermal expansions, elastic and creep properties of the various stack components. Knowing these, it is possible to estimate the stress evolution over time by a thermo-mechanical model. It is however essential that the *initial* stress field generated through the assembly of the SOFC stack is accurately determined.

To determine the initial stress field, the creep through the assembly of all the stack components is of key importance, as the stress development depends on the mutual relaxation of stresses. In this study we focus on the creep and relaxation of the stresses of the anode and anode support of the SOFC as this, for many cell designs, constitutes the main structural component. The anode/anode-support is typically made from nickel (Ni) and zirconia with 3 or 8 mol % yttrium doping.

Recently a phenomenon, so-called *accelerated creep* of SOFC Ni(O)-YSZ anodes occurring on the reduction of the NiO, has been discovered [1]. The creep phenomenon was studied by measuring macroscopic deflections/extensions of composite samples on different sequences of loading and reduction. Different creep rates were found in bending and uniaxial tension. The reason for this was speculated to be due to a chemo-mechanical interaction, i.e. mechanical stress nucleates the chemical reduction, which as a consequence occurs faster on stressed zones. A hypothesis for the mechanisms behind the accelerated creep was also proposed, i.e. it is due to a fast softening of the Ni(O) phase during reduction, which provides; 1) increased creep rate of the relatively porous YSZ backbone, 2) a significant decrease of the elastic modulus (by a factor of 10), 3) an expansion due to release of compressive residual stresses in the YSZ phase. The latter is contradicting previous literature but is confirmed by measurements. It also implies that the internal residual stress between the Ni(O) and YSZ phases, arising from the cool down after sintering, are completely released upon reduction (see Fig. 2).
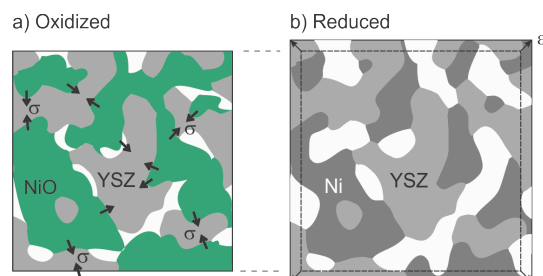

Fig. 1. Expansion of microstructure during reduction due to release of residual stresses.

Residual stresses in NiO-YSZ half cells have been measured by X-ray diffraction by following the Bragg edges for different reflection angles at room temperature, see e.g. [2–4], from the curvature of half-cells and by modelling it by creep deformations from the sintering temperature [3,5].

In this work the residual stresses (/elastic strains) are measured by *in-situ* XRD as a function of temperature in oxidized (as sintered) condition and through reduction.

II. Experimental

Samples were tape-cast and sintered half-cells consisting of a ~300 μm anode support of NiO-3YSZ, ~40 μm anode of NiO-8YSZ anode, and 10 μm electrolyte.

The *in-situ* X-ray diffraction measurements were carried out in a Rigaku SmartLab diffractometer with Cu Kα radiation, using an Anton Paar HTK 1200N high temperature oven chamber with atmosphere control. The XRD patterns were recorded in the 2θ range 25 – 150° with a step of 0.01°. The software package PDXL was employed for the Whole Powder Pattern Fitting of the diffractograms and for the microstrain analysis based on the Halder-Wagner method [6].

III. Results

In Fig. 1 the elastic microstrain in both phases of the composite measured through the heat up of the oxidized (as sintered) anode support and during cooling after reduction is plotted. The elastic strain is directly proportional to the stress (with elastic modulus as proportionality factor). Through the reduction the stress drops in both material phases and goes to zero in the Ni phase. Some stress remains in the YSZ phase.
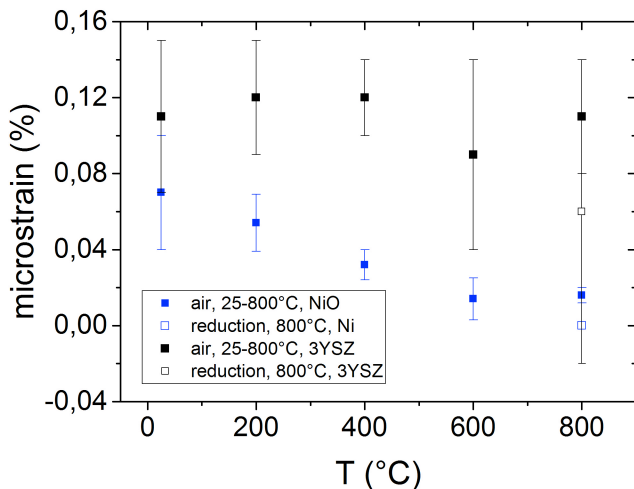

Fig. 2. Microstrain of the individual phases of the Ni(O)-3YSZ composite through temperature and reduction.

IV. Discussion

That the stress in Ni(O) phase goes to zero at reduction is consistent with the hypothesis for the expansion during reduction in [1] (see Fig. 1). That the stress in the YSZ phase in the anode support does not go to zero at reduction could be ascribed to the small TEC difference between 3YSZ and 8YSZ in the different half-cell layers. Further work is under way to record XRD data with improved signal to noise ratio in an attempt to reproduce these results and reduce the uncertainty of the estimated microstrain values.

The measured elastic strain is related to the previous estimates of expansion of the YSZ backbone through reduction (0.04 % at 800ºC), as the expansion at this point is exactly due to the release of residual stresses (according to the hypothesis

in [1]. By extrapolating this residual strain linearly to room temperature given a reference temperature of ~1100ºC results in a strain of 0.11 % (0.04 % × 800ºC / 300ºC), which is in very good agreement with these measurements (see Fig. 2).

This means that for a SOFC constrained in a stack the elastic expansion of the YSZ during reduction will be balanced by the other stack components through the seals. If a particular stack design has problems with durability of the seals, reduction of the SOFC stack should be considered immediately after sealing the stack, as the seals might at this point be ductile and compliant to release the compressive residual stresses in the YSZ phase (in electrolyte and anode).

In general the observed phenomenon complicates a thermo-mechanical simulation of a SOFC stack considerably, as the phases of Ni-YSZ layers in principle must be considered individually. However, in many cases it is reasonable to assume that all stress goes to zero in the SOFC stack at the point of reduction (see above discussion), which simplifies the thermo-mechanical analysis.

V. Conclusion

In this work the elastic microstrain was measured up through temperature in oxidized condition, through reduction at 800ºC. The stress in the Ni phase goes to zero during reduction, which is consistent with previously reported macroscopic expansions on reduction of Ni(O)/YSZ-composites. These expansions are one of the contributions of the large distortions occurring during reduction of the composite, referred to as accelerated creep.

Furthermore, the amount of residual microstrain in the YSZ was found to be in the order of 0.11 % at room temperature, which is in very good agreement with the observed expansion on reduction in the previous work [1].The consequence of this is that the stress in many cases can be considered to go to zero at the point of reduction in SOFC stacks.

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