Final report for PROSOFC

1.1 Project details

Project title	Production and Reliability Oriented SOFC Cell and Stack Design (PROSOFC)
Project identification (program abbrev. and file)	12236
Name of the programme which has funded the project	ForskEL together with Fuel Cell and Hydrogen – Joint Undertaking (FP7, EU)
Project managing company/institution (name and address)	Henrik Lund Frandsen, Technical University of Denmark (DTU) In EU: Martin Hauth, AVL, Austria
Project partners	Technical University of Denmark (DK) In EU: AVL (AU), Dynardo GmbH (AU), SOLIDpower S.p.A (IT), Karlsruhe Instiute of Technology, KIT (DE), Forschungszentrum Jülich, FZJ (DE), Imperial College, IC (GB), École Polytechnique Fédérale De Lausanne, EPFL (CH), Joint Research Center, JRC (B)
CVR (central business register)	30060946
Date for submission	

The current report will focus on the contributions from DTU, but they will be framed in the context of the EU project, as DTU's role is on supplying the scientific foundation for the EU project (together with others).

1.2 Short description of project objective and results

1.2.1 In the EU project

The objective of the EU project is to improve the robustness of the solid oxide fuel cell (SOFC) technology through modifications of the stack manufacturing and design at a SOFC stack manufacturer, SOLIDpower. The method was adopted from the car industry, where Dynardo for years have utilized the cost-optimal reliability-based design (COPRD) approach. This dertermines impact to design modifications by a multiphysical model (made by EPFL) of a SOFC stack exposed to operational scenarios (set by AVL – integrator). The scientific foundation for the models was supplied by KIT (on electrochemistry), IC, FZJ and DTU (on solid mechanics).

The model framework with the COPRD and the complex multiphysics model was constructed. Based on this SOLIDpower identified design changes to improve the robustness of their SOFC stacks, and increased the maximum number of deep thermal cycles from 50 to 120, an essential parameter for dynamic operation.

1.2.2 In the Danish supplementary project

The objective of the Danish project is to supply the scientific foundation on the mechanical behaviour of SOFC stack components. In the EU project this was done in collaboration with FZJ and IC. The focus for DTU is on the SOFCs themselves and the steel interconnector.

DTU investigated mechanical behaviour of those at room temperature as well at operation conditions (~800°C and reducing atmosphere). Strength, elastic properties and creep properties was measured and microstructural models was used to understand the intrinsic interplay between phases leading to the effective macroscopic properties (e.g. strength of anode support, and creep of interconnect component). A particular interesting finding is a special very fast creep phenomenon in the SOFCs occurring during assembly. It was found that creep relaxes practically all the residual stresses in the cells during reduction. This has thus significant impact on the integrity of the SOFC stacks.

1.3 Executive summary

The objective of the EU project is to improve the robustness of the solid oxide fuel cell (SOFC) technology through modifications of the stack manufacturing and design at a SOFC stack manufacturer. Initially, Topsøe Fuel Cell A/S was the stack manufacturer in the project, but with their closure in 2015, SOLIDpower S.p.A. replaced them in the project. This transition in the consortium required some throttling of the project, and in the end an extension of it.

The project was led by AVL, a larger Austrian company with roots in the car industry, i.e. on powertrain development and test systems towards, in particular towards the needed robustness. The robustness optimization of the SOFC stacks was thus done through requirements partially specified by them as integrator and partially specified by the stack manufacturer.

The optimization was done in two steps; 1) through simulations and virtual optimization and 2) by implementation in the production at the SOFC stack manufacturer and consequent testing of stacks.

Dynardo GmbH lead the work on simulation and robust optimization with methods also adopted from the car industry, i.e. cost-optimal reliability-based design (COPRD). Here they used a statistical approach, where variations in the production are accounted for in the optimization, in order to achieve a robust design (such that small variations in production do not impact the robustness significantly). In the first step they identified sensitivities to changes in the SOFC stack design and in the second step they optimized the SOFC stack. Both steps required a model of the SOFC stack, with the ability to predict the response to design changes. This was supplied by TOFC in the first part of the project and EPFL in the second part.

For the stack models to be truly predictive, the physical properties was measured at the relevant conditions. These measurements should also be able to reflect the variations occurring in the production (porosities, geometry). Especially the electro-chemical and solid mechanics behaviour of the SOFCs and other stack components were in focus in the project. KIT together with the different stack suppliers investigated the electro-chemical performance. The solid mechanical investigations was undertaken by IC, FZJ and DTU, and headed by DTU.

IC college focused on fracture and residual stresses in the glass sealings. FZJ focused on the creep of the SOFCs together with creep and the strength of the glass sealings. The focus for DTU was on the SOFCs themselves and the steel interconnector.

DTU measured the strength of the SOFC anode support (main structural layer) at different temperatures (from RT to 800°C) and in different atmospheres (air and diluted hydrogen). The strength in hydrogen varied significantly with temperature. By studying the residual stresses on the microstructurel level of the anode support of the SOFC, it was found to increase significantly towards room temperature. Based on this a hypothesis for the strength variation was postulated. DTU also measured the creep properties of the cell, and a special creep phenomenon occurring during the assembly of the SOFC stacks was discovered. Further investigations showed that the stresses in the anode support during reduction almost relaxed to zero. This is important for the understanding of the safety margins to avoid cracking of the cell during operation, because the result is that the protective compressive residual stresses in the electrolyte are relaxed as well.

Another line of work for DTU was on the creep of the interconnect and the steel material, they are made of. The transient primary creep properties was measured for the first time due to novel equipment devised in the cause of the project. The equipment involves a line laser shining through a furnace for accurate displacement measures. The creep measurements was described by a mathematical material law (constitutive law) in order to simulate the behaviour of it in a SOFC stack model. The material model was also used to estimate the creep properties of the entire interconnect, which is a corrugated steel plate. The re-occuring geometry was further used to develop a method to effectively model the interconnect with an immense computational gain. The method involved so-called homogeneziation, which allows omitting geometric sub-mm features in a SOFC stack of several (10-20) cm in all three dimensions.

EPFL used the homogenization approach in their stack models to simulate the stacks of SOLIDpower. EPFL also based their models on the assumption that the stress was relaxed upon reduction, as shown in DTU's work. The stack models was used together with COPRD (supplied by Dynardo). This was used to study design changes in SOLIDpowers stack. The new stacks was tested by SOLIDpower and AVL also tested the stacks from SOLIDpower.

An example for a specific outcome of the project was that SOLIDpower increased the maximum number of deep thermal cycles from 50 to 120, an essential parameter for dynamic operation.

1.4 Project objectives

The Danish supplementary project had identical objectives as the European project, where DTU was involved (primarily WP2 and WP9). The European project was modified slightly with the entrance of the SOLIDpower and EPFL, halfway in the project. In the European project, DTU was involved in the following deliverables and milestones (final version):

1.4.1 Deliverables

D2.1 Technical report and data files for material models based on current production (DTU, M12)

D2.3 Technical report on complex creep behaviour of the SOFC materials (DTU, M54)

D9.1 Report on 1st invited workshop on SOFC mechanics (DTU, M15)

D9.3 Report on 2nd invited workshop on SOFC mechanics (DTU, M48)

1.4.2 Milestones

M2.1: Refined continuum material models formulated and ready for stack modelling (DTU, M12)

M2.2: Recommendations for production based on detailed sealing failure studies (DTU, M54)

M9.1 1st invited workshop on SOFC mechanics (DTU, M15)

M9.3 2nd invited workshop on SOFC mechanics (DTU, M48)

1.5 Project results and dissemination of results

In the first part of the project, the stack manufacturer, was Topsøe Fuel Cell (TOFC), which was closed half-way in the project. Their main interest was the behaviour of the ceramic cells, and DTU characterized the strength and creep properties of these at operational conditions. This work is reported in section 1.5.1 and 1.5.2-1.5.3, respectively.

With the closure of TOFC, SOLIDpower stepped into the project as a stack provider, and with this a slight redefinition of the project was made. The task for DTU did however remain largely the same, namely to characterization of the interconnect steel components, as this also had the interest of SOLIDpower. This is work is reported in section 1.5.5 to 1.5.6. Furthermore, additional studies on the impact of the discovered phenomenon, Accelerated Creep, was defined for the latter part of the project – reported in section 1.5.4.

1.5.1 Measurement of cell strength

SOFCs are subjected to significant stresses from the handling during production and thermal gradients during operation. To set the limit for which operational conditions can be allowed before failure, the strength must be known at the relevant operational conditions.

In the project the strength of the main structural component of the SOFC, i.e. the NiO-YSZ anode support was thus studied under various conditions and pre-treatments.

1.5.1.1 The effect of pre-treatment

Before operation, the cells must undergo a chemical reduction (NiO-YSZ -> Ni-YSZ) to be functional in the stack. The effect of the chemical reduction temperature was known to influence the electro-chemical performance of the cell, but the influence of reduction temperature was unknown. In the project this was studied by measuring the strength at high temperature in a in-house constructed rig with the capability to measure a large number of samples by four point bending [1]. This is needed to correctly represent the statistical distribution of strength. The 63 % fractile of the measured strengths is known as the Weibull Strength.

In Figure 1 the Weibull strength is shown as a function of the reduction temperature. It is found that the highest strength is achieved, if the cells are reduced at 900°C.

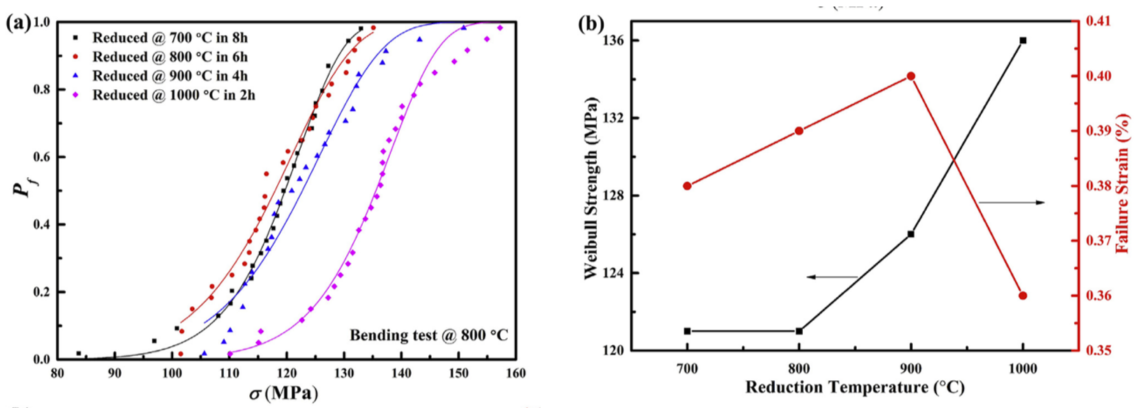

Figure 1 (a) Weibull plots showing the distribution of strength for Ni YSZ anode sup- ports reduced at different conditions; (b) The variation of Weibull strengths and failure strains as a function of reduction temperature for the reduced Ni YSZ anode sup-ports[2].

1.5.1.2 Strength variations with temperature

The strength of the anode supports were measured at every 200°C between root temperature (RT) and 800°C in the oxidized (NiO-YSZ) and reduced condition (Ni-YSZ). More than 30 samples were measured at each temperature. The variation of elastic modulus (stiffness), Weibull strength and failure strain with temperatures is shown in Figure 2. The resuts in Figure 2 leads to the to following findings:

- When in the oxidized all ceramic state, the stiffness ands strength are incensitive to temperature.
- In the reduced state the Ni softens with temperature, lowering both the stiffness and the strength.
- The strength of the oxidized anode support is considerable stronger than the reduced. This is mainly attributed to the porosity, which increases with the reduction (NiO->Ni).
- The reduced anode support can be strained (elongated) more than the oxidized, and is thus more forgiving in terms of thermal gradients.

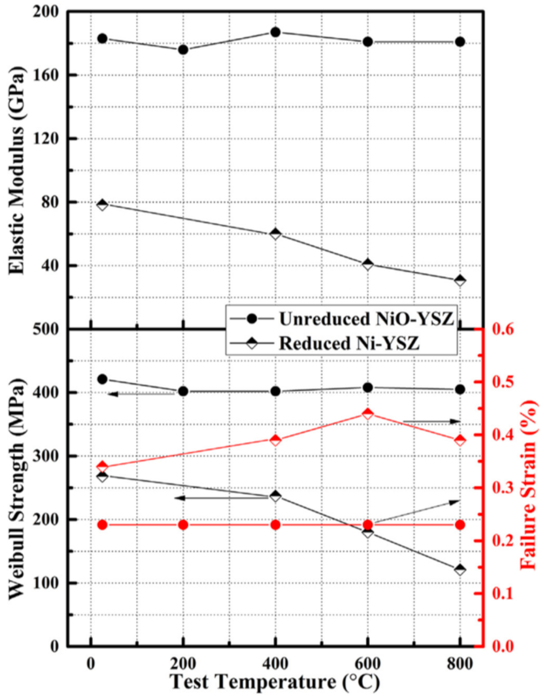

Figure 2 Weibull plots showing the distribution of strength for the reduced (a) and unreduced (b) Ni(O)-YSZ anode supports over the temperature range from room temperature to 800°C. All the Ni-YSZ specimens were reduced at 800°C in 6 h [2].

This data together with literature data formed the basis of the D2.1, and the achievement of M2.1.

1.5.2 Impact of creep on the probability of failure of an SOFC stack

To predict possible failure with the SOFC stack models in WP4, the mechanical material parameters must be known. It is shown in ref. [1] that creep influence the stress in the SOFC stacks over time and thus influence the probability of failure of the cells, see Figure 3. Here the probability of failure is seen to peak, when the operational conditions are changed. Between shifts in operation the stress relaxes governed by the new temperature distribution.

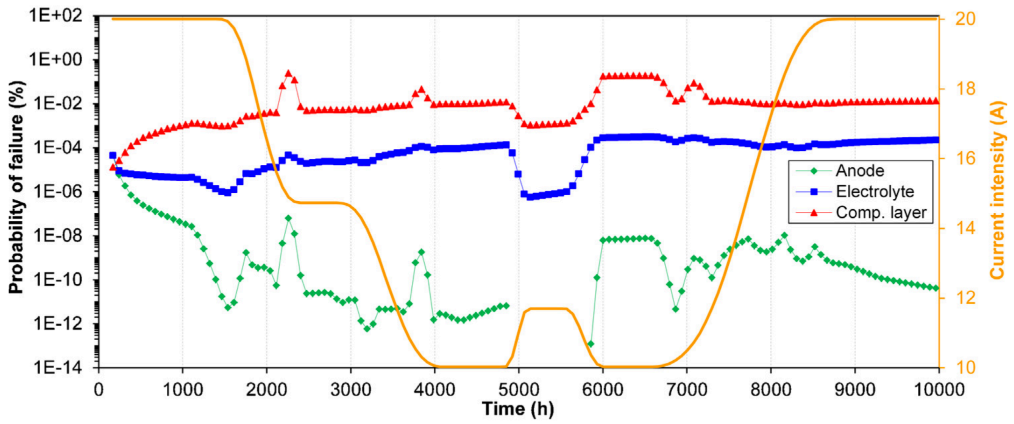

Figure 3 Probability of failure of the different layers of a SOFC stack as a function of time and changes in current intensity [1].

The conclusion of this that the creep rate and strength has a significant impact on the probability of failure, and must be characterized well. The purpose of WP2 is to determine the creep properties and strength of the main structural components of the SOFC, i.e. the anode support of the cell, the sealings, and the interconnector steel.

1.5.3 Discovery of Accelerated Creep phenomenon

In the project a phenomenon, 'accelerated creep' in Ni(O)-YSZ anode supports, was discovered. The phenomenon takes place during the reduction of the fuel cell.

In Figure 4 the displacement over time at the centre of an anode support sample in three-point bending is shown. The accelerated creep is resulting in the fast displacement at reduction (steep drop of curve). This occurs under constant load at the shift of atmosphere around the sample from air to a mixture of 9%H_2 in N_2, which reduces the sample.

The accelerated creep is approximately 10^4 times faster than creep during operation. The creep phenomenon is also seen to be concentrated in time, i.e. within 5-10 minutes. This corresponds to the estimated time for reducing the anode.

To exclude effects of asymmetric reduction and loading (in bending), creep experiments were also conducted in uniaxial tension, as show in Figure 5. From this it can be concluded:

- Combined loading and reduction 1) in Figure 5a result in much faster and larger elongations as compared to a number of 'reference cases' 2)-5) [4].
- Even complete removal of Ni, leaving a much more open structure 4), did not produce as high creep rates than the accelerated creep.
- Reduction before loading 3) gave a non-negligible but not as large creep response.
- Reducing the sample for 10 minutes before loading 2) provided intermediate amount of creep, due to partial accelerated creep.

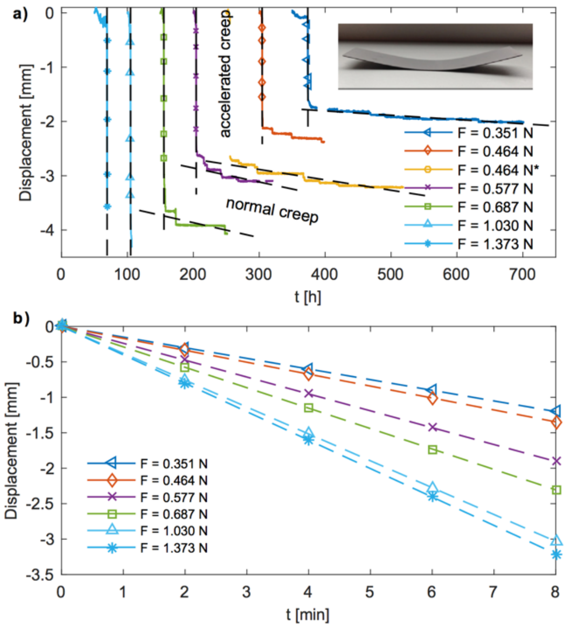

Figure 4 a) Displacement of the center of beams exposed to different loads in three-point bending and a shift of atmosphere from air to 9%H2 at 800°C (resulting in accelerated creep). A close up on the steep decent during accelerated creep (marked with x's) are in b). The insert in a) shows the curvature of a sample after creep testing [4].

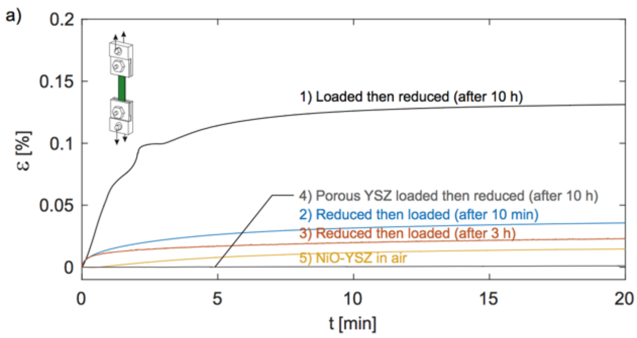

Figure 5 Creep strain over time for different initiations of uniaxial loading relative to the initiation of the reduction (red.) at 2 MPa of load. The insert illustrates the fixture used for the experiments [4].

Conclusively, it can be stated that the accelerated creep occurs at the combination reduction and loading, independent of loading method. The hypothesis for the occurrence of the phenomenon is that the Ni softens significantly during reduction, decreasing the load bearing capacity to nearly zero. This stresses the YSZ backbone further, inducing a fast primary creep in this phase. Furthermore, significant drop of elastic stiffness and release of residual stresses are also partial explanations for the large deformations, see ref. [4] for further details. As loading and reduction occurs at every SOFC stack assembly, this phenomenon has a significant impact stresses in the beginning of the SOFC stack life and onwards.

1.5.4 Relaxation of stresses during SOFC stack assembly

To investigate the impact of the accelerated creep phenomenon on a SOFC stacks, the stresses during heating, under reduction and during cooling was measured in-situ by use of x-ray diffraction (XRD). This was done both on at macro-scale, i.e. studying the stresses in a half-cell (anode+electrolyte), and on a micro-structural scale.

1.5.4.1 Macro-scale measurements of stresses by XRD

The distance between the crystal planes, of the ceramics in an SOFC, are increased when exposed to stress. To determine the stresses in the layers of an SOFC (anode and electrolyte) X-ray diffraction is used to estimate the distance between crystal planes at zero stress (perpendicular to the cell plane) and at an angle where lattice planes are distorted due to stress, see Figure 6. For further details, please refer to ref [5].

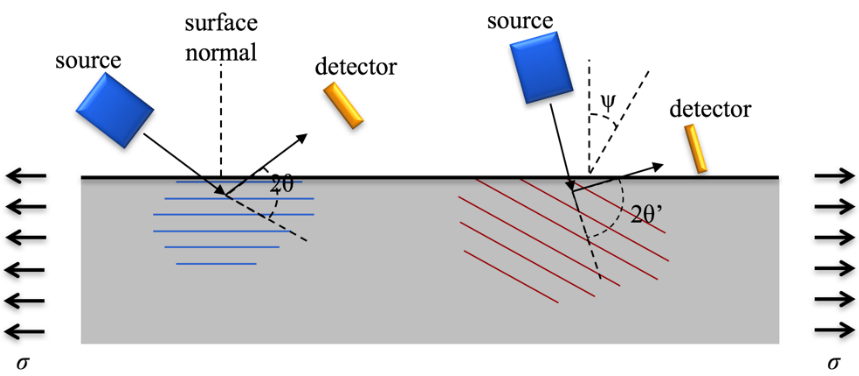

Figure 6 Schematic representation of XRD-based measurement of in-plane residual strain[5].

In Figure 7 the in-plane residual compressive stress in the 8YSZ electrolyte layer decreases monotonously upon heating in air to 700 °C. At 700°C the remaining stress is drastically relaxed from -168± 10 MPa upon reduction in 9% H_2 (3% H_2O, 88% N_2) at 700 °C to -30 ± 19 MPa. Compressive stress builds up again in the 8YSZ layer upon cooling in the same reducing environment, but at a slower rate.

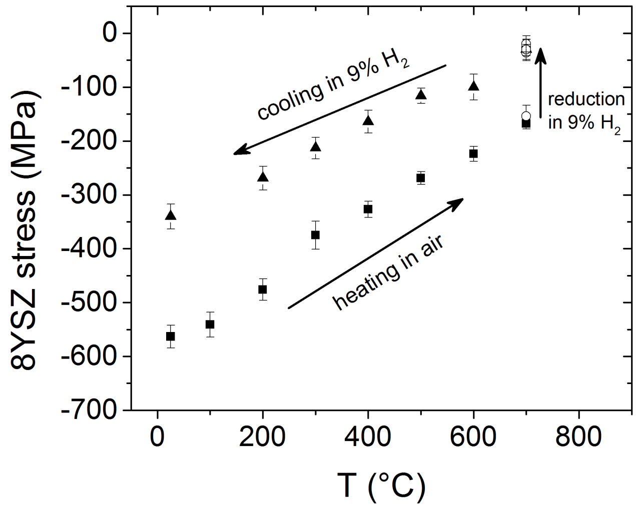

Figure 7 Evolution of in-plane residual stress in the 8YSZ electrolyte layer of the HC sample upon heating in air to 700 °C, reduction in 9% H2 (3% H2O, 88% N2), and cooling in the same reducing environment[5].

The evolution of in-plane stress in the 8YSZ electrolyte was explored upon heating in air to different reduction temperatures of 600, 700 or 800 °C [5]. Relaxation was found with some variations in results, but with one main conclusion: the stresses drastically decreases during reduction of the NiO to Ni at higher temperatures. This is attributed to fast chemically activated creep of Ni(O) at the typical reduction temperature of 800 °C.

These findings thus also confirm part of the hypothesis for explaining the previously observed so-called "accelerated creep". This entails that the stress in the SOFC practically is zeroed at the point of reduction. This has a great impact on the understanding of the stress evolution in a SOFC stack, both during assembly but also during reduction. Because until now the understanding was that the electrolyte was under a protective compressive stress. This is however now known to vanish during the reduction of the SOFC.

1.5.4.2 Micro-scale measurements of stresses by XRD

The anode material is being considered as a single layer, but is a composite of Ni and YSZ, with different physical properties. The two phases are intrinsically joined and influence each other when exposed to external exposure, such as temperature changes or loading. Thus, when cooling the composite from their sintering temperature (where they are joined) stresses will build up as they have different thermal expansion coefficient. The stress build up will put one phase in compression (YSZ) and the other in tension (Ni). The strength of the composite is believed to rely on the ceramic YSZ (the Ni will not break, just yield plastically). Thus, the bigger the compressive stress build up in the YSZ, the larger the tensile stress is needed to break the composite.

In the project the micro-strain in each phase of the composite Ni(O)-8YSZ fuel electrode is determined by in-situ X-ray diffraction before, during and after reduction from the widening of the Bragg peaks due to local stress. The broadening of the Bragg peaks does not reveal whether these strains are extensions or compressions, but from the CTE of the materials, we presume that 8YSZ will be compressed and NiO extended.

In Figure 8 the evolution of micro-strain NiO-8YSZ sample exposed to increasing temperature in air and upon reduction and cooling in 9% H_2 (3% H_2O, 88% N_2) is presented. The trend is the same as for the macro-stress in the electrolyte. During the reduction the stress drops and increases as the sample is cooled, but not at the same rate.

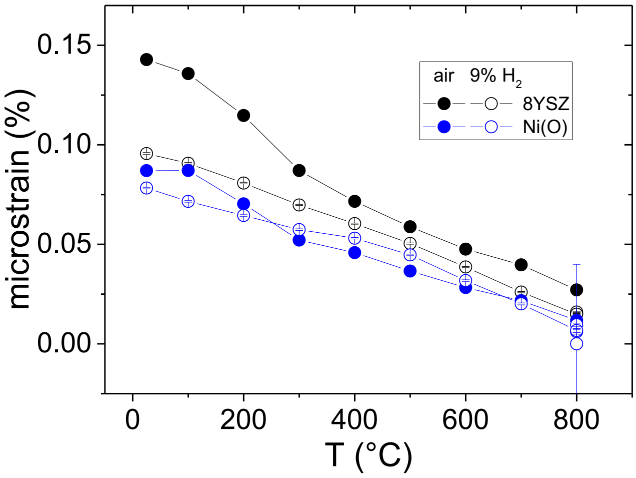

Figure 8: Evolution of micro-strain in the 8YSZ and Ni(O) phases of the NiO-8YSZ tape casted and sintered sample with increasing temperature in air and upon reduction and cooling in 9% H_2 (3% H2O, 88% N2) [5].

To better understand the process of micro-strain build-up upon cooling, this has also been assessed by micro-mechanical modelling on the basis of a 3D reconstruction of the micro-structure, see Figure 9. The model includes the thermal contraction, elastic response as well as creep and plasticity. In Figure 9 the stresses are furthermore seen to peak at the interface between the Ni and YSZ, due to the mismatch in thermal contraction.

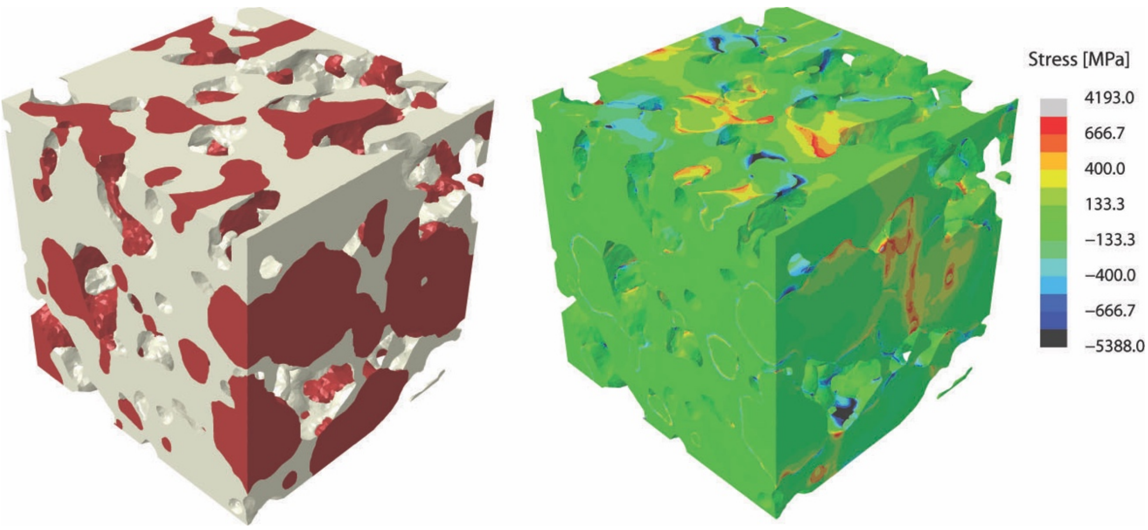

Figure 9: Stress distribution in the Ni-8YSZ microstructure at 0 ℃ (right). The undeformed configuration is included on the left to show phase distribution (Ni in red and 8YSZ in white)[6].

The microstructural model predicts the micro-strain variation during the cooling of the Ni-YSZ composite shown in Figure 10. The magnitude of the micro-strain variation compares well to that of the measurements. The model do however predict the strain building up slower in the beginning (at higher temperatures) and faster towards the end.

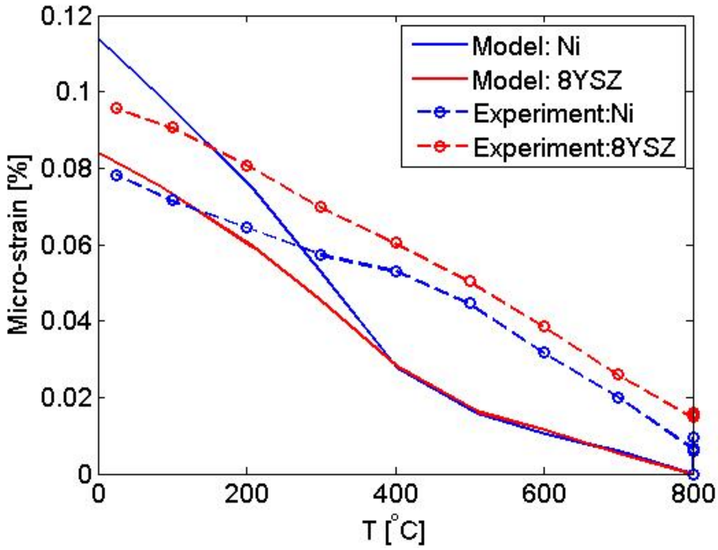

Figure 10: Comparison of Ni and 8YSZ micro-strains between micromechanical modelling and X-ray diffraction experiments during cooling from 800 °C.

In the PROSOFC project it was found that the Weibull strength of Ni-YSZ increased by 148 MPa (from 124 MPa to 272 MPa) when going down in temperature from 800 °C (after reducing at 800 °C), see Deliverable 2.1 and ref. [7]. This could also very well be due to increasing residual compressive stresses build up in the YSZ phase when going down in temperature, which was found in this micro-structural simulation to be -149 MPa.

The model used for the microstructural simulation of the Ni-YSZ structure during cooling was originally developed to describe the creep at high temperature in the composite in ref. [3]. Here it was found that the creep of the composite was highly depending on the YSZ phase, as this in creep is significantly stiffer than the Ni phase. For this reason, it was also concluded that creep rate of the composite depends on the effective amount of YSZ phase and that the Ni phase can be considered as porosity. Finally, by comparing the numerical homogenization prediction and existing analytical models showed that the Ramakrishnan–Arunchalam creep model captures the relationship between creep factor and porosity most closely, while all other models have underestimated the increase in creep rate, see Figure 11.

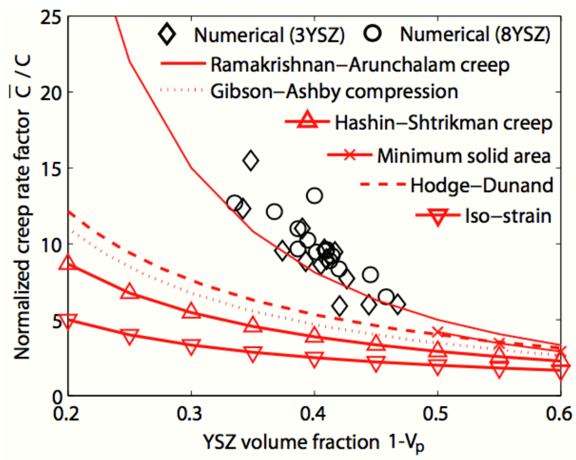

Figure 11 Normalized creep rate determined by microstructural modelling (◊ and O) compared to analytical models from the literature [3].

1.5.5 Computational efficient modelling of creep of interconnects

Thermo-mechanical analysis of the entire solid oxide fuel cell (SOFC) stack at operational conditions is computationally challenging if the geometry of metallic interconnects is considered explicitly. This is particularly the case when creep deformations in the interconnect are considered in addition to elasticity. In the project this is addressed by using a mathematical abstraction of the actual geometry, i.e. homogenization. By this method, the effect of the geometry is built into an "effective anisotropic material law" for a continuum block of material, which then represents the interconnect in the stack model.

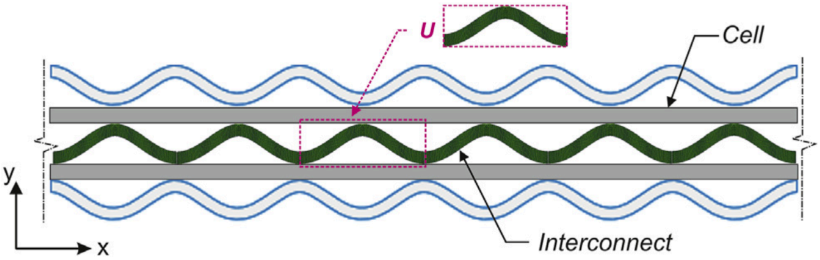

Figure 12 Schematics showing the cross sectional view of interconnects and electrode structures[8].

This is done by a finite element model of a part of the actual repetitive geometry and from this deduct a constitutive law for the homogenized structure (effective material law). In order to properly describe the mechanical behaviour of the interconnect at high temperature, deformations involving the elastic, creep as well as effect of changes in the geometry due to contact is accounted for. The constitutive law can be applied using 3D modelling, but for simple presentation of the theory, 2D plane strain formulation is used to model the corrugated metallic interconnect, see Figure 13.

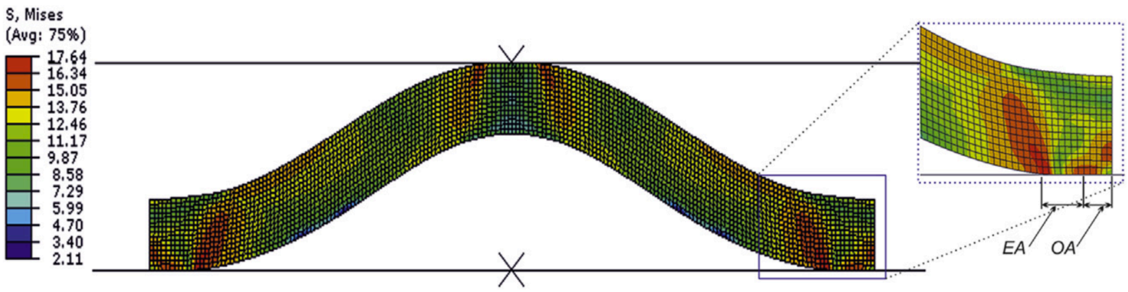

Figure 13 Solution of a unit cell model showing the distributions of local von Mises stresses[8].

The mathematical material law (constitutive law) reminds of that of an anisotropic creep law, with a state variable accounting for the distortion of the microstructure, please refer to ref. [8] for further details.

In Figure 14, the developed constitutive law is verified by comparing its predictions for creep strain with results from the original 2D finite element model for different loading conditions. Further examples can be found in ref. [8]. The constitutive law is found to describe both the initial non-linear contacting and linear steady state creep reasonably.

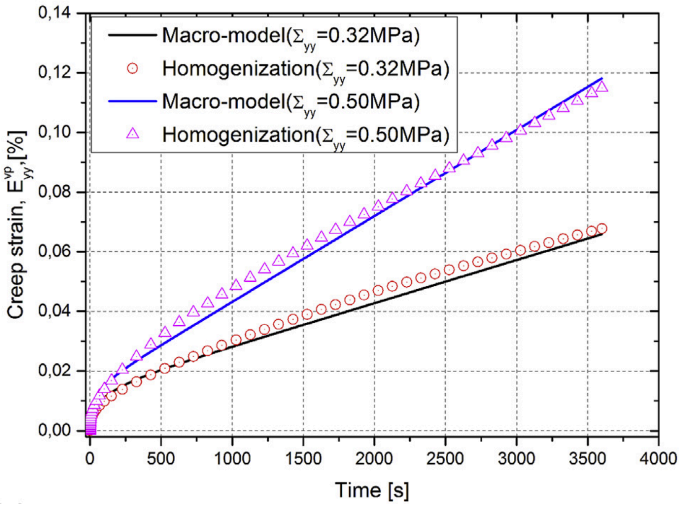

Figure 14 Comparison of average creep strains from the microstructural model and the homogenized model under load in the vertical direction.

The result of this work is thus that a very complex geometry can be considered in a mechanical model of SOFC stack with tremendous computational gains and with a satisfactory description of the macro-scopic deformation in the stack.

1.5.6 Measurement of transient creep of interconnect steels

In the project, an experimental method for in-situ measurement of the transient creep response at operational conditions is developed[9]. This method is used to characterize the creep response of a commonly used commercial steel, Crofer 22 APU, at operational conditions[10]. To utilize these measurements to predict the stresses and the integrity of a SOFC stack, a mathematical material model is further developed to describe the measured response[10].

1.5.6.1 Development of measurement method

The methodology for measuring the transient creep uses a mechanical loading rig designed to apply variable as well as constant loads on samples within a gas-tight high temperature furnace. In addition, a remotely installed length measuring setup involving laser micrometer is used to monitor deformations in the sample in the furnace. The method is developed based on constructing a combination of existing equipment.

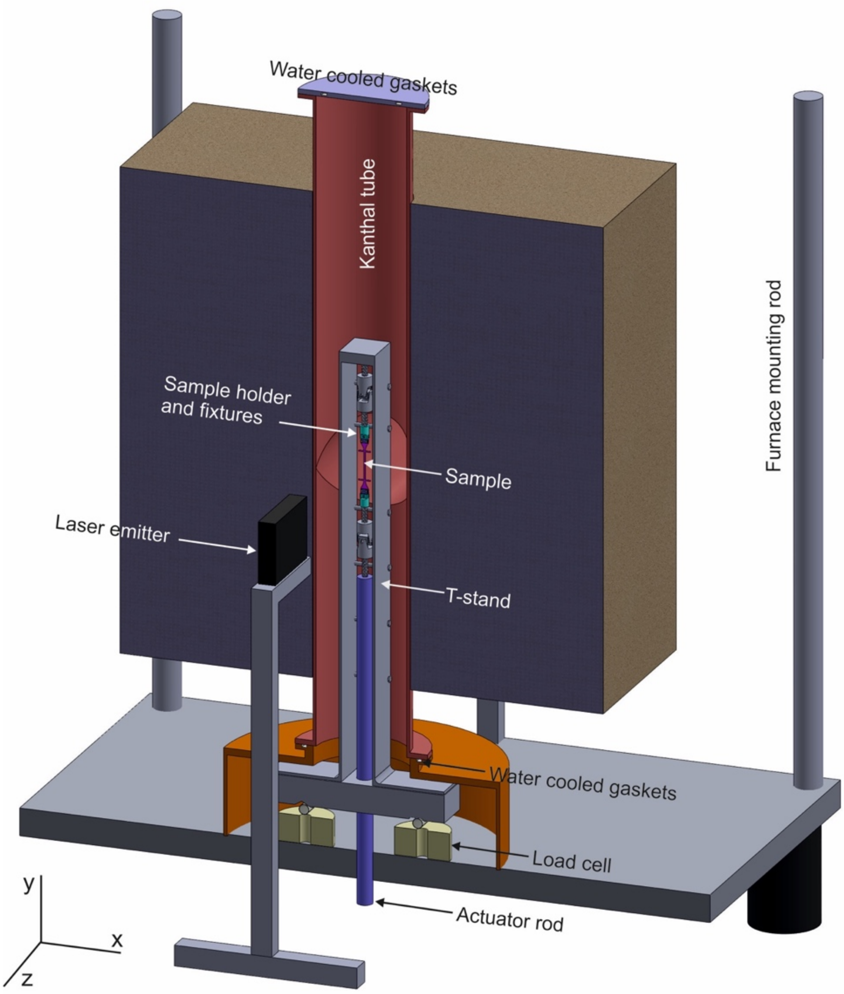

Figure 15 3D schematic representation of the main parts of the experimental facility (sectional view)[9].

To avoid friction from parts moving in and out of a gas-tight high temperature furnace, load cells (measures load) are placed within the same environment as the sample. The setup does however ensure a low temperature at the load cells, by controlling convection, conduction as well as radiation away from the load cells, such that these are at tolerable temperatures. For further details, please refer to references [9,11].

The extension is measured by using a line-laser shining through the furnace through two port-holes, sealed with glass windows, see Figure 16. The laser gauges the length of the sample, from the shade of the two flaps on the sample, see Figure 17. Figure 17 also illustrates the mounting of the sample.

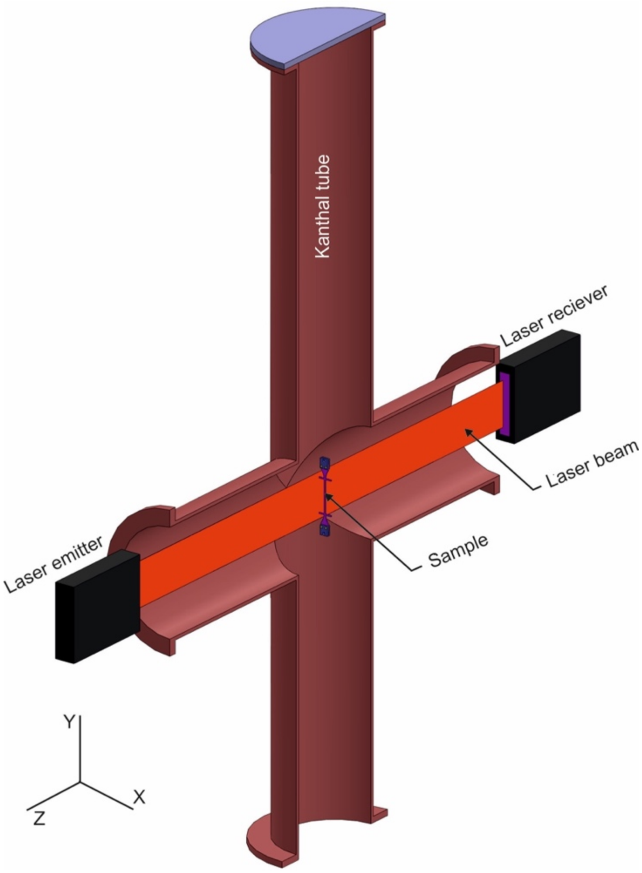

Figure 16 Schematic representation showing sectional view of the cross shaped Kanthal tube together with the positions of laser micrometer setup and test sample[9].

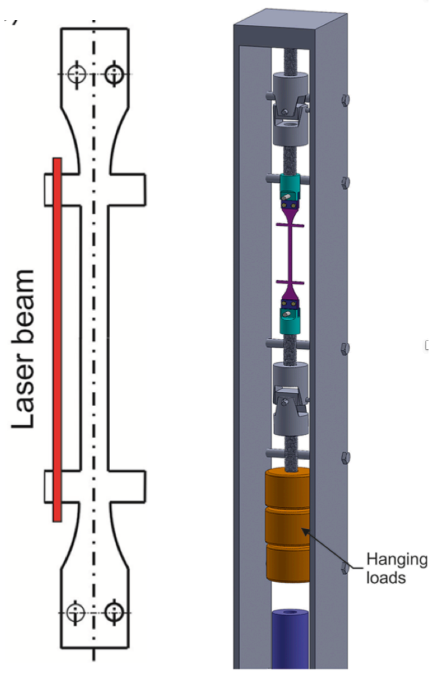

Figure 17 Sample with laser beam from laser micrometer and mounting of sample in fixture[9].

With the setup the deformations within the furnace is thus measured relatively accurately, i.e. with an error as low as 2-3 μm, resulting in an error on the strain of ~0.01 %.

With his equipment primary creep strain, constant strain rate (Figure 18a), and relaxation (Figure 18b) can be recorded with high accuracy in-situ.

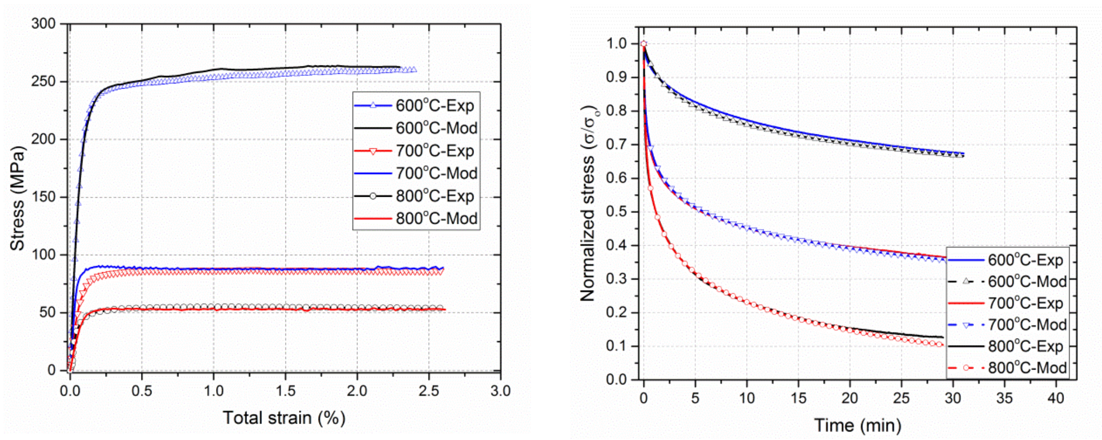

Figure 18 (a) Comparison of constant strain rate behaviour of Crofer 22 APU at different temperatures [stroke rate = 0.12 mm/min] (b) Relaxation behaviour of Crofer 22 APU at different temperatures[10].

1.5.6.2 Mathematical modelling of primary creep of interconnect steels

To utilize the measurements recorded by the high temperature creep measurement equipment described in previous section (1.5.6.1) in SOFC stack models in the PROSOFC project, these must be described by a mathematical material model (constitutive law). In the project it was thus investigated whether a further development of the so-called Chaboche's unified power law together with isotropic hardening can represent the transient behaviour of Crofer 22 APU, see ref. [10].

The material parameters for the model are determined by measurements involving relaxation and constant strain rate experiments (see Figure 18). The stress relaxation experiments show a rapid change in high-temperature softening of Crofer 22 APU above 700°C.

In order to validate the model, a user defined material (UMAT) is developed to implement the constitutive law using commercial finite element software, ABAQUS^{TM}. The model output was thus cyclic loading experiments (Figure 19a) and creep experiments (Figure 19b) - with the material parameters extracted in the constant strain rate and relaxation experiments (Figure 18).

During creep tests, it was also observed that significant creep non-linearities (primary creep) occur at 600°C compared to cases at 700 and 800°C. Based on these results it was concluded that creep deformation of Crofer 22 APU at 600 °C is dominated by primary creep.

(a) (b)

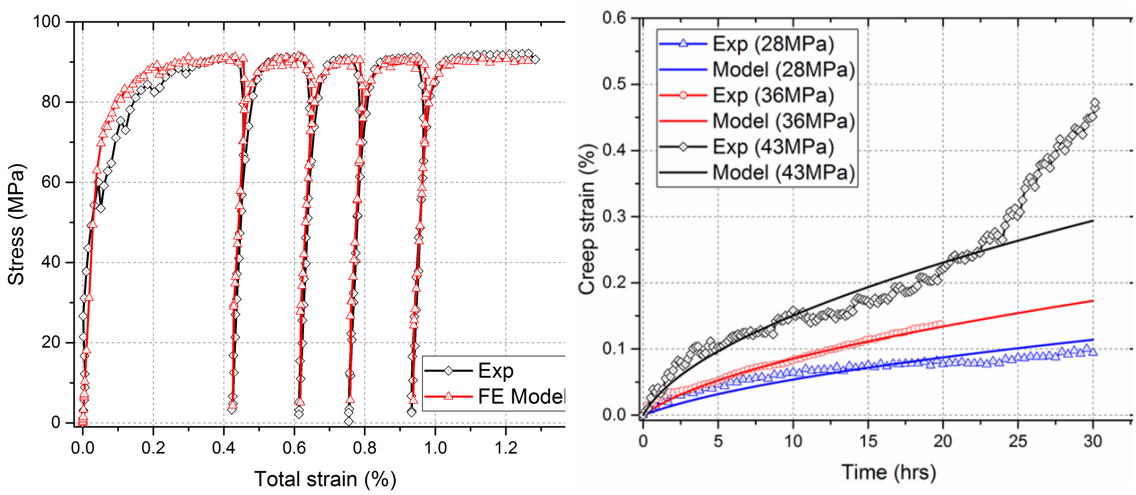

Figure 19 (a) Comparison of experimental measurements and model prediction for Crofer 22 APU under cyclic loading at 700 °C [stroke rate =0.12 mm/min] (b), (b) Comparison of experiment versus model for creep behaviour of Crofer 22 APU at 600 °C.

It was found that the developed constitutive model reasonably captures the experimental measurements during cyclic loading as well as creep tests at three operational temperatures of SOFCs. It is therefore concluded that Chaboche's unified power law with modifications can be applied to describe the high temperature inelastic deformational behaviours of Crofer 22 APU used for metallic interconnects in SOFC stacks.

1.5.6.3 Abnormal creep behaviour of commercial interconnect steels

Different steel compositions are used by different SOFC stack manufacturers. The creep properties were only known for steady state creep for a few (Crofer 22 APU and Crofer 22 H, ThyssenKrupp, Germany). In the project the transient primary creep steel of the stack manufacturer in the PROSOFC project, SOLIDpower, was investigated and compared to the two commercial alloys Crofer 22 APU and Crofer 22 H from ThyssenKrupp.

In Figure 20 the primary transient creep behaviour of the three different steels are compared through two load cycles, stressing the steel with 12 MPa. Transient creep is present in both load cycles, and the quite commonly used alloy, Crofer 22 APU, is seen to creep significantly faster than the Crofer 22 H and the steel of SOLIDpower. The laves phases, segregating at the grain boundary junctions, are known to minimize the creep response of the Crofer 22 H. Similar microstructure could be the reason for the SOLIDpower steel to be equally creep resistant as the Crofer 22 H (this is however confidential).

The steel of SOLIDpower also seems to have another unique feature; it contracts after half an hour to one hour while being exposed to tensile loading. The mechanism for this contraction is also unknown, but rather interesting. It could be due to release of residual stresses during the manufacturing (e.g. cold rolling) or perhaps growth of laves phases during the first heating after manufacturing.

(a) (b)

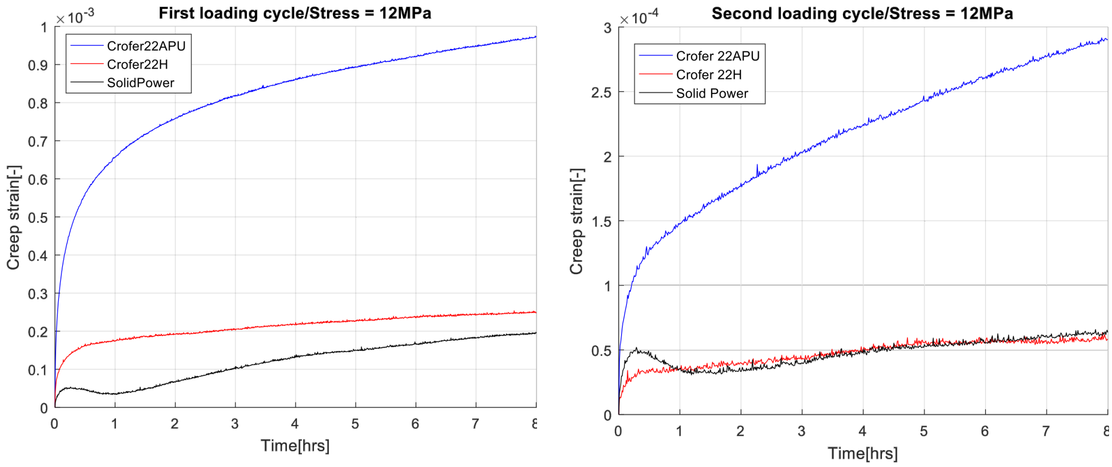

Figure 20 Transient primary creep at 700°C of Crofer 22 APU, Crofer 22 H and the steel used by SOLIDpower, during (a) the first loading cycle and (b) second loading cycle.

With some annealing (35 hours at 700°C), this effect can be partially removed as seen on Figure 21. To elucidate this abnormal behaviour further research is however needed.

(a) (b)

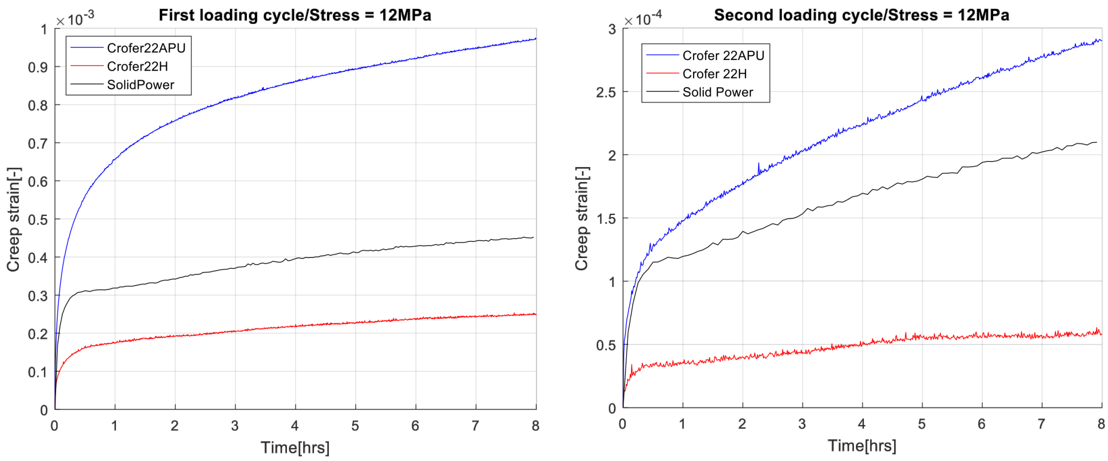

Figure 21 Transient primary creep at 700°C of Crofer 22 APU, Crofer 22 H and the steel used by SOLIDpower after annealing for 35 hours at 700°C, during (a) the first loading cycle and (b) second loading cycle.

D2.3. was based on: 1) the creep behaviour of the cell described in Section 1.5.3 and the resulting relaxtion described in Section 1.5.4, 2) the creep behaviour of the interconnect described in Section 1.5.6 and the modelling thereof in Section 1.5.5 and 1.5.5, and 3) creep measurements of the anode support and glass sealing by FZJ and EPFL.

1.5.7 *Dissemination*

1.5.7.1 Media coverage

At project initiation a journalist working for Danmarks Radio became interested in the technology and interviewed Henrik Lund Frandsen about the PROSOFC project and wrote an article on the basis [11], see Figure 22.

This attracted some attention from interested Danes as well as from abroad.

Figure 22 Print of header of the DR Viden article on SOFCs in connection with the PROSOFC project.

1.5.7.2 International Workshops on Mechanics in SOFCs

Two international workshops have been held in connection with the European Fuel Cell Forum (EFCF) in Lucerne, Switzerland in 2014 and in 2016. The participants came from both acadamia as well as the industry from Europe and USA, with a total number of participants of 26 and 20 at the two workshops.

The overall topic of the workshops was on improving the mechanical robustness of the SOFC technology, in-line with the objective of the PROSOFC project. At the first workshop in 2014, the focus was on:

- Part I: Mechanical challenges for the SOFC technology – where should we use fracture mechanics and statistical approaches, respectively
- Part II: How to capture important phenomena in SOFC modeling with current computational power available

In 2016 the topics were:

- Part I: Brittle interfaces in SOFC stacks – the best tools to characterize and analyze them
- Part II: Flexible or rigid material components to fight the thermal stresses – guides to the engineers

Further details on the workshops can be found in D9.1 and D9.3 of the European PROSOFC project. With the completion of the two workshops, M9.1 and M9.3 were fulfilled.

Figure 23 Picture from Workshop 1 in 2014.

Figure 24 Picture from Workshop 2 in 2016.

The workshops allowed for a good desimination of the the ongoing work in PROSOFC project as well as input from external experts.

At the first workshop in 2014 in particular Edgar Lara-Curzio from Oak Ridge National Laboratory, USA gave valuable feedback to some of the mechanical testing methods applied in the project in terms of suggestions for improvements. In the workshop Briggs White, US DOE National Energy Technology Laboratory, USA (responsible for the SECA program, USA) found the collaboration between industry and academia interesting.

The second workshop in 2016 led to some interesting discussions regarding general views on stack designs. The FZJ Jülich participants (Ludger Blum, Jürgen Malzbender) mostly believed in using creep resistant materials in all components, whereas the representative from SOLIDpower, Zacharie Wuillemin, believed that some of the components of the stack should be flexible to accommodate thermal stresses (without specifying which). Generally, it can be concluded that this certainly deserves more attention from the research community.

1.5.7.3 Scientific papers

The work described in the previous sections has been reported in scientific international peer-reviewed journal papers, i.e. references [2,3,6,8–10], while two papers is yet to be submitted [4,5]. Also a number of conference proceedings papers have been written on the topics reported here, i.e. references [12–16].

[1] H.L. Frandsen, D.J. Curran, S. Rasmussen, P.V. Hendriksen, High throughput measurement of high temperature strength of ceramics in controlled atmosphere and its use on solid oxide fuel cell anode supports, J. Power Sources. 258 (2014) 195–203. doi:10.1016/j.jpowsour.2014.02.036.

[2] D.-W. Ni, B. Charlas, K. Kwok, T.T. Molla, P.V. Hendriksen, H.L. Frandsen, Influence of temperature and atmosphere on the strength and elastic modulus of solid oxide fuel cell anode supports, J. Power Sources. 311 (2016) 1–12. doi:10.1016/j.jpowsour.2016.02.027.

[3] H.L. Frandsen, M. Makowska, C. Chatzichristodoulou, F. Greco, D.W. Ni, D.J. Curran, M. Strobl, L. Theil Kuhn, P.V. Hendriksen, Accelerated creep in solid oxide fuel cell anode supports during reduction, J. Power Sources. 323 (2016) 78–89.

[4] H.L. Frandsen, C. Chatzichristodoulou, B. Charlas, R. Kiebach, K. Kwok, P. Norby, P.V. Hendriksen, In-situ determination of strain evolution in Solid Oxide Cells upon reduction. Part I: In-plane residual macro-strain in the cell layers, (2017).

[5] C. Chatzichristodoulou, K. Kwok, B. Charlas, R. Kiebach, P. Norby, P.V. Hendriksen, H.L. Frandsen, In-situ determination of strain evolution in Solid Oxide Cells upon reduction. Part II: Micro-strain within Ni(O) and YSZ in the fuel electrode, (2017).

[6] K. Kwok, P.S. Jørgensen, H.L. Frandsen, Computation of effective steady-state creep of porous Ni-YSZ composites with reconstructed microstructures, J. Am. Ceram. Soc. 98 (2015) 1–8.

[7] F. Greco, H.L. Frandsen, A. Nakajo, M.F. Madsen, J. Van herle, Modelling the impact of creep on the probability of failure of a solid oxide fuel cell stack, J. Eur. Ceram. Soc. 34 (2014) 2695–2704. doi:10.1016/j.jeurceramsoc.2013.12.055.

[8] T.T. Molla, K. Kwok, H.L. Frandsen, Efficient modeling of metallic interconnects for thermo-mechanical simulation of SOFC stacks: Homogenized behaviors and effect of contact, Int. J. Hydrogen Energy. 41 (2016) 6433–6444. doi:10.1016/j.ijhydene.2016.03.002.

[9] T.T. Molla, F. Greco, K. Kwok, P. Zielke, H.L. Frandsen, Development of high temperature mechanical rig for characterizing the viscoplastic properties of alloys used in solid oxide cells, J. Test. Eval. (2017).

[10] T.T. Molla, K. Kwok, H.L. Frandsen, Transient deformational properties of high temperature alloys used in solid oxide fuel cell stacks, J. Power Sources. 351 (2017) 8–16. doi:10.1016/j.jpowsour.2017.03.059.

[11] H. Kokkegård, Fremtidens brændselsceller holder til alt, DR Viden. (2013).

[12] K. Kwok, P.S. Jørgensen, H.L. Frandsen, Micromechanical Modeling of Solid Oxide Fuel Cell Anode Supports based on Three-dimensional Reconstructions, in: Proc. 11th Eur. SOFC SOE Forum 2014, 2014, Eur. Fuel Cell Forum, 2014.

[13] D.W. Ni, B. Charlas, K. Kwok, H.L. Frandsen, Mechanical Properties of Ni-YSZ Anode Materials for Solid Oxide Fuel Cells, in: 39th Int. Conf. Expo Adv. Ceram. Compos., 2015.

[14] B. Charlas, C. Chatzichristodoulou, K. Brodersen, K. Kwok, P. Norby, M. Chen, H.L. Frandsen, Residual stresses in a co-sintered SOC half-cell during post-sintering cooling, in: N. Christiansen, J.B. Hansen (Eds.), 11th Eur. SOFC SOE Forum 2014, Lucerne, 2014: p. B1107.

[15] H.L. Frandsen, C. Chatzichristodoulou, P.V. Hendriksen, Complete Relaxation of Residual Stresses During Reduction of Solid Oxide Fuel Cells, in: V. Cigolotti, C. Barchiesi, M. Chianella (Eds.), Proc. EFC2016, Italian National Agency For New Technologies, Energy And Sustainable Economic Development, Naples, Italy, 2015.

[16] Henrik Lund Frandsen, C. Chatzichristodoulou, P.S. Jørgensen, K. Kwok, P.V. Hendriksen, Relaxation of stresses during reduction of anode supported SOFCs, in: N. Brandon (Ed.), Proc. 12th Eur. SOFC SOE Forum 2016, 2016: pp. B11-17-B11-23.

1.5.7.4 Conference presentations

The work was also disseminated through presentations at a number of international conferences:

1. Henrik Lund Frandsen, "Accelerated creep of Ni-YSZ anodes during reduction" , European Fuel Cell Forum 2014, Lucerne, Switzerland
2. Benoit Charlas, "Residual stresses in a co-sintered SOC half-cell during post-sintering cooling", European Fuel Cell Forum 2014, Lucerne, Switzerland
3. Kawai Kwok, "Micromechanical modeling of porous ceramic composites using microstructural reconstructions", Energy Marterials and Nanotechnolgy meeting on Ceramics, 2015, Orlando, USA
4. De-Wei Ni,. "Influence of operational conditions on the strength of SOFC anode supports", 39th International conferencen and expo on advanced ceramics and composites, 2015, Daytona Beach, USA
5. Henrik Lund Frandsen, "Complete Relaxation of Residual Stresses During Reduction of Solid Oxide Fuel Cells", European Fuel Cell 2015, Napoli, Italy
6. Christodoulos Chatzichristodoulou, "Thermo-Chemo-Mechanical Response of Solid Oxide Cells during Reduction and Cooling", 229th ECS Meeting, 2016, USA, San Diego

7. Tesfaya Tadessa Molla, "Computational efficient thermo-mechanical modelling of interconnects in SOFC stacks including the effect of contact" Energy Challenges and Mechanics Symposium 2016, Inverness, Scotland, UK
8. Henrik Lund Frandsen, "Complete Relaxation of Residual Stresses During Reduction of Solid Oxide Fuel Cells", European Fuel Cell Forum 2016, Lucerne, Switzerland

1.6 Utilization of project results

The result of the work described in Section 1.5 of the Danish complementary project financed by ForskEL was utilized directly in the EU project, in particular in WP4, where the material data and behaviour was used to simulate the operation of an SOFC stack.

The homogenization models developed and described in Section 1.5.5 was further used in a EUDP project on electrolysis stacks, "Maturing SOEC" (project number 64015-0523) to simulate the long-term mechanical influence of thermal gradients across a SOC stack.

The developed testing method and models are now also available for both national and international partners, and will be utilized in upcoming projects.

1.7 Project conclusion and perspective

In the PROSOFC project broad fundamental knowledge on the mechanical behaviour of materials at high temperature and in various atmosphere has been established. This ranges from extensive characterization with e.g. more than 3000 samples tested to characterize the statistical variation of strength to new phenomena as accelerated creep. To perform the measurements at operational conditions (high temperatures, reducing atmospheres) novel equipment have been established; for strength testing and for creep testing.

The results have been published in international peer reviewed scientific journals (6 papers published two more to be submitted) and in conference proceedings (5 papers). The topic of the project was also covered in the media, DR Viden.

The outcome of the Danish complementary project was directly utilized in the EU project to optimize the design of SOLIDpower's SOFC stacks. Based on this SOLIDpower was amongst others was able to double the number of deep thermal cycles before failure, a parameter essential for dynamic operation of the SOFC technology.

Where SOFC technology currently is lessed addressed in a Danish context with the closure of TOFC, the sibling, solid oxide electrolysis cells (SOEC) technology, is still being developed and recently also commercialized by Haldor Topsøe A/S for on-site manufacturing of CO. Due to the technologies high efficiencies, fuel flexibility and tolerance to impurities, these migh very well play an essential role in the future Danish energy system, in particular for storage of energy, upgrade of biogas and/or synthetic fuel production.

Therefore the project results are also used in an ongoing EUDP project on the SOEC technology together with Haldor Topsoe A/S, "Maturing SOEC" (project numer: 64015- 0523), and will be available in national as well as international upcoming projects.

Annex

http://prosofc-project.eu