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Synopsis   Results of the first in-situ energy resolved neutron imaging of NiO-YSZ reduction under applied stress are presented. Neutron experiments were performed at the pulsed neutron source ISIS (UK) using a time-of-flight (TOF) approach.

Abstract   This work reports on in-situ macroscopic scale imaging of NiO-YSZ reduction under applied stress – a phase transition taking place in solid oxide electrochemical cells in reducing atmosphere of hydrogen/nitrogen mixture and at operation temperatures of up to 850 ℃. This process is critical for the performance and lifetime of the cells. Energy resolved neutron imaging was applied to observe the phase transition directly with time and spatial resolution. We present two different approaches for using this imaging technique for the investigation of chemical and physical processes requiring controlled atmosphere and elevated temperature. The first type of measurement is based on alternating stages of short-term partial chemical reaction and longer neutron image acquisition, and the second type is a real in-situ neutron imaging experiment. Results of applying energy resolved neutron imaging with both approaches to the NiO-YSZ reduction investigation indicate enhancement of the reduction rate due to applied stress, which is consistent with the results of our previous research.

Keywords: Energy resolved neutron imaging; SOFC anode supports, in-situ phase mapping.

1. Introduction

Solid oxide cells (SOC) offer a prominent technology for the future energy conversion of excess electricity to chemical energy (e.g. in fuels) or storage by reversible operation. Ni-YSZ cermet is the state-of-the-art material for production of electrodes and mechanical supports of solid oxide electrochemical cells (SOCs)(Hauch et al., 2008; Malzbender et al., 2009; Laguna-Bercero, 2012). One of the most promising production methods for commercial planar cells is tape casting from a NiO-YSZ slurry, since it is a relatively cheap process that can be applied for large scale production (Ramousse et al., 2007). Tape casting is followed by sintering, and subsequently in the first hours of operation of an SOC, NiO-YSZ layers are reduced to Ni-YSZ cermet. It has been shown that this initial process is crucial for the SOC properties and performance during the entire operation cycle as well as for its lifetime (Moseley et al., 2011; Frandsen et al., 2016).

Observation of the phase transition during reduction of the NiO-YSZ composite into Ni-YSZ cermet has been of great research interest for decades since it is related not only to chemical changes but also to severe microstructural changes in a combination that so far is not understood in detail. Further, the SOCs are subject to stress while operating in a stack configuration, and there are indications that the stress is also linked to the phase transition (Frandsen et al., 2016). Numerous experimental techniques have been applied for ex-situ investigations of this process (e.g. XRD, SEM, EDS (Malzbender et al., 2005; Modena et al., 2006; Tikekar et al., 2006; Li et al., 2010)). Recently, also in-situ experiments were presented: S. B. Simonsen *et al.* have presented environmental TEM studies of morphology changes in NiO-YSZ during reduction(Simonsen et al., 2014, 2015); K. V. Hansen et al. reported on in-situ observation of reduction in NiO-YSZ-Al_2O_3 composites performed using a controlled atmosphere high-temperature scanning probe microscope (CAHT-SPM)(Hansen et al., 2014) . These techniques give an insight into the processes at the nano- or microscopic scale; however, they are invasive and require model samples that can't mimic the additional influence of stress.

Many scientific reports present also studies of Ni-YSZ cermet using macroscopic techniques, e.g. impedance spectroscopy (Li et al., 2010; Vladikova et al., 2015), dilatometry (Pihlatie et al., 2007), thermogravimetry (Modena et al., 2006; Yoshito et al., 2009; Pihlatie et al., 2010). These methods can potentially be performed in-situ, however they do not provide direct local information about phase content and distribution, as the achieved information is averaged for the whole sample.

The effect of stress on the reduction of NiO-YSZ has been studied most recently together with the newly found phenomenon of accelerated creep (Frandsen et al., 2016). In this work it was revealed that the influence of stress on the reduction process of NiO-YSZ for SOC applications is not fully understood and it can have a great impact on the residual stresses in the SOFC cells and stacks after reduction. Hence, in-situ studies of this relation are important and of high relevance for the robustness of SOC technology.

Neutron imaging (Strobl et al., 2009; Kardjilov et al., 2011) is a non-invasive measurement technique allowing for detecting and distinguishing Ni and NiO phases with spatial resolution on a macroscopic scale throughout the volume of bulk samples. Moreover due to the high penetration power of neutrons, such measurements can be performed using a sample environment providing conditions required to conduct the reduction process, meaning that neutron imaging of NiO-YSZ reduction can be performed in-situ. Up to now, the application of neutron imaging has been limited by the currently available instrumentation and neutron fluxes, i.e. with respect to resolution in time and space. However, the recently developed and introduced neutron detection technology utilizing Boron doped Micro Chanel Plates (MCP) together with the TimePix technology (Tremsin et al., 2011, 2012, 2013, 2014) and a custom designed sample environment (Makowska et al., 2015c) created opportunity for in-situ energy resolved neutron imaging of chemical processes like NiO-YSZ reduction.

At pulsed neutron sources e.g. ISIS (RAL, UK), pulses of white neutron radiation are generated, and neutrons of different energies (and hence velocities) reach the sample and the detector at different times. MCP detectors are able to record the intensity of the beam transmitted through the sample with high spatial and time resolution. The latter allows discretization of neutron wavelength information from the arrival time of neutrons at the detector, which is referred to as time-of-flight (TOF) method. Together with the spatial resolution, it enables energy resolved neutron imaging. Measured transmitted beam intensity I values are converted to the macroscopic cross section values Σ using Lambert-Beer law: $I/I_0 = \exp(-\Sigma d)$, where I_0 is the incident beam intensity and d is the sample thickness.

Using the TOF method, patterns illustrating the dependence of the macroscopic cross section of a material on the neutron wavelength, are acquired (Kockelmann et al., 2007). For polycrystalline samples, such patterns contain distinct edges occurring for neutron wavelengths λ, which, according to Bragg's law, correspond to crystal lattice spacing values d_{hkl} as $\lambda=2d_{hkl}$ for the largest possible Bragg angle of $\theta = \frac{\pi}{2}$. Therefore, from these - so called - Bragg edge patterns, information about crystallographic characteristics of the investigated material can be extracted (Josic et al., 2011; Sato et al., 2011; Kardjilov et al., 2012; Strobl et al., 2012; Woracek et al., 2014). In particular, for materials containing several different crystalline phases, their content can be evaluated. In our earlier work on phase mapping in NiO-YSZ composites at different stages of reduction, an algorithm for quantitative evaluation of Ni and NiO phase contents was presented (Makowska et al., 2015b). In (Makowska et al., 2015b), mapping of a corresponding reduction degree, which was defined as normalized NiO phase mass loss in time, was presented as well.

In this work, the MCP detectors and a custom designed sample environment were utilized to apply energy resolved neutron imaging for the observation of the NiO-YSZ reduction process. In particular the reduction process and the influence of mechanical stress on this process were studied.

2. Experimental

The preparation of samples for the presented experiments was similar to the procedure described in more detail in references (Makowska et al., 2015a; b): several layers of 300 μm thick tape cast NiO-YSZ tape were stacked together, hot-pressed at 130 ^{0}C and sintered at 1400 ^{0}C. The obtained layers were laser cut to dimensions 20 x 7 x 1 mm^{3}.

The utilized sample environment, which is described in (Makowska et al., 2015c), was specifically designed for in-situ high resolution neutron imaging studies of processes requiring elevated temperature (up to 1100 ^{0}C) and switching between various controlled atmospheres (in this case so-called safety gas 9% H_2 with 91% N_2, air and N_2, but other gases can also be applied). This furnace also enables placing the sample in close proximity to the neutron detector, which is critical for achieving sufficient spatial resolution in a neutron imaging set-up where finite beam divergence can blur the resulting image. In this experiment, samples were placed 30 mm from the MCP detector.

Energy resolved neutron imaging measurements were performed at the Rutherford Appleton Laboratory (UK) at the pulsed neutron source ISIS, utilizing the Engin-X instrument (Daymond & Edwards, 2004; Zhang et al., 2013). Engin-X is a neutron diffractometer used mainly for material science and engineering. Using an MCP detector with 55 μm pixel size, available at Engin-X, energy resolved neutron imaging experiments are possible.

Here we present spatially and time resolved studies of the reduction reaction in NiO-YSZ under applied load, as stress is always present in real stacked SOCs, and because according to previous research a strong correlation between reduction rate and stress is expected (Frandsen et al., 2014, 2016; Makowska et al., 2015b). It has been demonstrated in (Frandsen et al., 2016) that during reduction under applied load significant creep – so called "accelerated creep"- is observed, leading to a large sample deformation. During the in-situ experiments presented here, the samples were placed horizontally in a fixture inside a sealed quartz tube, in which the gas atmosphere could be controlled with constant flow. One side of the sample was fixed in the holder and the other side of the sample acted like a cantilever beam, which was mechanically loaded with forces acting in vertical direction (figure 1 b). This results in a bending moment on the sample, which internally distributes stresses along the axial direction of the sample (tension in the top and compression in the bottom, figure 1 c). A more detailed description of the sample holder can be found in (Makowska et al., 2015c).

Measurements were performed using two different approaches, referred to as "in-situ" and "stop-and-go" experiments. In the first type of experiments ("in-situ"), neutron imaging measurements are performed during the reduction process. The experiment was performed in the following steps:

- Heating of the loaded sample to the target temperature in N_2 atmosphere with a flow of 120 l/h.

- Neutron image acquisition for the initial state while the sample was held at the target temperature.

- Introducing reducing gas (9% H_2 with 91% of N_2) with flow of 100 l/h, simultaneously starting acquisition of neutron images every 2-3 minutes (2 min for $T=650^0C$ and $T=800^0C$ and 3 min for $T=600^0C$). A longer exposure time per image was chosen at 600^0C because of the significantly slower reduction rate at this temperature.

In the second type of experiments ("stop-and–go"), neutron image acquisition was performed before and between consecutive steps of short time partial reduction. In other words, the reduction was conducted analogically to the in-situ experiments, but for a short time, then the reaction was stopped, followed by a long term (>30 min) acquisition of neutron images of the sample in the "frozen", partially reduced state. This procedure was repeated several times with different time spans of chemical reaction steps ranging from 1 minute to 20 minutes. Images were acquired more often in the beginning of the process, when the reaction rate is faster. The reduction reaction was interrupted after each step by simultaneously switching to N_2 and fast cooling to room temperature. Cooling rate was not controlled, but a temperature of around 300 ^0C, at which the reduction process stops completely, was reached in about 1.5 min.

Energy resolved neutron imaging is a technique, which can be applied to in-situ studies, but the time resolution depends on the neutron flux at the sample position (the source power, beam collimation), instrument characteristics, sample size and material as well as on the quantity/parameter that is to be probed and the spatial resolution required. In particular, for the samples measured in this experiment and for the information sought in this work, an approximate time resolution of about 30 s can be achieved only at the brightest neutron sources.

A compromise between spatial resolution and image integration time is to be found in most experiments as the neutron flux at available neutron imaging instruments is currently limited to $\sim 10^6$-10^8 $n/cm^2/s$. The time resolution required for the here introduced investigations of the NiO-YSZ reduction in the temperature range 650^0C -800^0C is on the order of at least 3 min. This is a challenging requirement for the present neutron beamline facilities and their specific instrumentation.

In our experiments the time resolution requirement was chosen prior to measurements according to the expected reaction rate. However, it turned out to be not sufficient for tracking the changes in the parts of the samples, which are moving due to creep during in-situ reduction, as our experiments reveal. Better time resolution can however be achieved at the expense of spatial resolution by averaging signal over larger area of the sample.

3. Results and discussion

The main advantage of the "stop-and-go" method is that the sample state and position does not change during image acquisition, and exposure time is not limited by the chemical reaction rate and required time resolution. Consequently acquisition may be as long as needed to achieve sufficient statistics in order to obtain well spatially resolved phase distribution information. In fact, the achieved statistics in our experiments is sufficient to quantify the phase distributions with full image resolution. Thus, this approach can be used for phase mapping not only at the brightest neutron sources. However, the process of stopping and restarting the reaction is expected to affect the observed reaction kinetics. Results obtained with the "stop-and-go" approach are presented in figure 1 d, which illustrates the successful mapping of the reduction degree in a sample reduced at 650 ^{0}C for different times of the reaction.

The reduction degree defined as NiO phase mass loss with time was evaluated from measured Bragg edge patterns using an algorithm described in detail earlier (Makowska et al., 2015b). Ibidem the relation between the Bragg edge height (difference of macroscopic total cross sections for the highest and lowest point of the Bragg edge) and the particular phase content was described. It has been shown empirically that the dependence of the heights of the measured Bragg edges on the phase amount can be fitted with a linear function, despite structural changes in the material such as, and in particular, its porosity. This empirically proven dependence is in a good agreement with the dependence that can be derived from the Lambert-Beer law (Makowska, 2016). The algorithm presented in (Makowska et al., 2015b) was used in this work for data analysis. Any changes of orientation or size of crystallites as well as multiple scattering did not have to be taken into account, because no hints could be found that these effects influence the absolute edge heights and thus the results of the analyses of NiO-YSZ reduction. This is not only supported by the fact that no significant relevant variations in the Bragg edge spectra during reduction were detected, but was proven by the independently measured phase contents in calibration measurements presented in (Makowska et al., 2015b).

Figure 1a presents the measured Bragg edge patterns for the sample presented in figure 1d, averaged over area A (figure 1b) for selected reduction times. The plots clearly show the changes in the Bragg edges induced by the phase transition from NiO to Ni (edges corresponding to NiO phase decrease and edges corresponding to Ni phase increase with time). Figure 2 presents the measured Bragg edge patterns for the sample presented in figure 1d, averaged over areas A, B and D (figure 1b) after 15 min of reduction. The mapping of the reduction degree was achieved by a corresponding pixel-wise evaluation of the reduction degree from the Bragg edge patterns obtained for every single pixels.

The reduction degree changes apparently faster in the centre part of the sample compared to the parts closer to the ends of the sample (parts marked as A and D in figure 1b).

The distribution of the axial component of the stress tensor evaluated for the initial state of the sample is presented in figure 1 c). This simulation was performed using the Comsol Multiphysics commercial

finite element software. In part B (figure 1b) to the right side of the sample fixed point, the stresses are highest (figure 1c) and also in this part the most significant bending due to creep is observed during reduction. In parts A and D (figure 1b) stresses are significantly smaller or negligible (figure 1c) and these parts also do not experience deformation. The corresponding reduction rates can be observed to be considerably smaller in these regions (figure 1d, figure 3). Moreover, the reduction rate on the right side of the sample (part D), where the load was fixed, was significantly lower than on the left side, where the sample was fixed in the holder. Both load and sample holder were attached to the sample identically and therefore the significant difference in reduction rates on both sides of the sample was not expected and cannot be explained at this stage. Understanding this effect might require additional studies. This measurement was repeated for other samples with the same result.

The "stop-and-go" approach strictly speaking is not a real in-situ method, as neutron images are not recorded while the chemical processes occur, and the main issue of this approach is a distortion of the processes due to interruption. This always implies potential additional phenomena affecting the reduction, such as additional residual stress field and microstructure development in the investigated material. In particular, during reduction of the NiO-YSZ composite, residual stresses, created in the course of the sample production e.g. from cooling or after sintering (performed at 1400˚C), are released going to the exposure temperature of 650-800 ˚C. In the "stop-and-go" experiment, while during interrupting and re-starting of the reaction, samples are exposed to thermal cycles. This causes additional residual stresses due to the thermal expansion coefficients (TEC) mismatch of the involved phases YSZ, NiO and Ni. As we presented before (Makowska et al., 2015a; b), there is a strong link between stress and reduction rate, and hence new residual stresses will affect the progress of reduction. The additional stress will however act in a temperature interval, where the reduction kinetics are less pronounced and the cooling period is relatively short compared to the time span of the reduction kinetics. This points to that the "stop-and-go" has an insignificant influence on the experiment, but a further assessment of the significance of the distortion of the process induced by the "stop-and-go" procedure and the impact on the reduction progress is challenging. Although the differences are clearly measured, a more detailed dedicated study would be required to quantify the deviations induced, as well as their underlying causes. Because the conditions applied during the reduction process i.e. heating/cooling rate, final temperature and atmosphere affect also the microstructure (porosity, particle size) of the Ni-YSZ cermet significantly (Ebbehoj et al., 2012), the "stop-and-go" procedure also affects the microstructure development of the cermet.

In contrast the conditions of the in-situ approach are much closer to real reduction conditions and much better resemble the reduction reaction conducted in real electrochemical cells.

A series of in-situ measurements at different temperatures were performed. Figure 4 presents the time dependent reduction degrees measured in-situ of the samples reduced at 600 ^{0}C, 650 ^{0}C and 800 ^{0}C under applied load averaged over the region of interest of the samples, as indicated in figure 1b with

"C" (a sum of A and B). For the analysis of the reduction process two consecutive images were averaged in order to improve statistics. Thus the reduction degree for the first step after the initial stage was calculated as an average from images for steps 0 (initial stage) and 1, the next one from images for steps 1 and 2, next 2 and 3 and so forth. Such a running average approach keeps the time binning at 2 min for 650 ^{0}C and 800 ^{0}C (3 min for 600 ^{0}C), although each step is an average over 4 min (6 min respectively).

The resulting curves in figure 4 exhibit a slightly different behavior than the exponential dependence presented in (Makowska et al., 2015b) during the very first minutes of the process. Relatively slow reduction rates apparent in this time range are the consequence of slow response to the change of gas, as in this case time t=0 refers to the moment of switching to reducing gas flow. Consequently, at the early phase of the reaction (up to 2 min), the concentration of hydrogen is smaller compared to the stable conditions in the remaining part of the experiment. The curves in figure 4 indicate that differences in hydrogen concentration play an important role at lower temperatures, while at 800 ^{0}C no significant delay in response to the gas change is observed.

The most important advantage of energy resolved neutron imaging is the possibility to quantify the presence of various phases in the sample with spatial resolution. This has been used in our experiment to evaluate and compare the reduction progress in different parts of the sample exposed to different stress values and experiencing different deformation. Due to the geometry of the sample fixture and according to the simulation, we expect to achieve the highest stresses in part B and relatively negligible stresses in part A of the sample (figure 1b) and c)). During reduction significant creep is observed in the samples and again due to the fixture geometry the sample shape in part A remains unchanged, while most significant stress / bending occurs in part B. The part D on the other hand experiences the strongest movement and dislocation and as these are significant during even single image acquisition it could not be analyzed reliably in this case.

The graphs in figure 5 a), b), and c) present reduction degrees against the reduction time evaluated for the specific regions of interest A and B from in-situ measurements. The relative errors of calculated reduction degree values were determined to be about 10%. This is the reason of reduction degrees higher that 100% for 800 ^{0}C. In all cases the reduction rate in region B was faster compared to the nearly stress-free and non-deformed part A of the sample. Differences between reduction rates in parts A and B are similar at all the measured temperatures and samples. The curves presented in figure 5 b) were evaluated for a sample reduced at the same temperature as the sample analyzed with "stop-and-go" approach (sample presented in figure 1 and 3). Using the "stop-and-go" method appears to significantly slow down the reaction. A reason can be found in reduction delays caused by the system response time for multiple gas exchanges required to stop and re-start the reaction for every measurement. The curves presented in figure 5 also show a higher significance of the difference

between the stressed and nearly un-stressed parts of the sample in the in-situ study as compared to the stop-and-go experiments.

The observation of accelerated reduction rates related to stresses is consistent with our previous preliminary ex-situ measurements presented in (Makowska et al., 2015b). While this phenomenon previously was observed by other means by H. L. Frandsen et al.(Frandsen et al., 2016), the presented measurements have confirmed its existence by a direct observation through in-situ imaging. Although the results imply and confirm the reduction rate enhancement due to an applied load, it is not obvious whether the increased reduction rates are due to stress or phenomena related to the "accelerated creep" occurring at micro- or nano-scale, or a combination of both.

Significant creep in the samples observed during reduction under applied load is a challenge for the analysis of in-situ data. It implies that the sample is partly displaced during image acquisition. Consequently the quantification of in-situ data during critical times of the process is problematic for the parts of the sample that are displaced the most. This issue is avoided using the "stop-and-go" method, and hence only for this approach the phase distribution and reduction rate could be analyzed for the whole samples (figure 1), and not only for the part that doesn't move during the experiment.

In particular for the in-situ studies higher neutron flux is desirable, in order to achieve better time resolution and get more insight in the mechanism of the studied process during its first minutes. Shorter exposures could also facilitate the analyses of moving parts of the sample, which were not achievable currently. At the brightest existing spallation neutron sources about an order of magnitude in flux could be gained at a comparable instrument. The acquisition times for the in-situ experiments used in the present study would provide comparable statistics to the presented data from the "stop-and-go" approach (acquisition time was 30 min). In this case in-situ studies could provide the full information required for such study straightforwardly. Additional gains will be achieved with an instrument that better matches the wavelength resolution requirements of our study e.g. at RADEN beamline (J-PARC) (Kiyanagi et al., 2011). Hence, there is considerable potential for future studies at the European Spallation Source (ESS), where the resolution can be tailored to the needs of a measurement (Strobl, 2009, 2015)

4. Conclusion

In this work in-situ and quasi-in-situ energy resolved neutron imaging of the phase transition process from NiO to Ni in Ni-YSZ composite during reduction under applied stress is presented. Experiments were performed at the Engin-X instrument at ISIS using our custom build sample environment. The phase transition taking place in the material used for solid oxide electrochemical cells in reducing atmosphere of hydrogen/nitrogen mixture at temperatures of 600 ℃, 650 ℃ and 850 ℃ was observed using two different approaches: a "stop-and-go" type of approach and in-situ neutron experiments. While it could be demonstrated that in-situ measurements of the phase transition are feasible, both

methods reveal their advantages and disadvantages for this particular study. However, when applied together, they provide complementary information for the studied processes, due to complementary strengths under the given experimental conditions. Hence it turned out favourable to apply both approaches.

A clear difference in reduction degree in different parts of each sample was observed due to differences in stress levels. The effect could be confirmed at different temperatures and the different reduction rates under these conditions could be studied. The fastest reduction was observed overall at the highest temperatures and spatially in the high stress regions of the samples. In order to better understand the correlation between reduction reaction and the effect of applied load, further studies e.g. with different load values need to be performed.

The reduction appeared to display the smallest rate in the region of the sample with lowest stress level and the biggest distance from the region of highest stress and creep. This region could currently only be studied with the "stop-and-go" approach. The "stop-and-go" approach provides slower rates and smaller differences in reduction between the stressed and non-stressed sample regions. The reason is most likely to be found in the discontinuity and corresponding in-homogeneity of conditions over time in this case. That renders the in-situ study more suitable and desirable to study corresponding phase transitions.

Preferably, such experiments should be performed at neutron sources providing a higher neutron flux, in order to achieve better time resolution and get more insight in the mechanism of the studied processes during its first seconds and in order to enable in-situ mapping of the reduction degree in a whole sample.

Figure 1 a) Bragg edge patterns for selected reduction times calculated for area A; b) scheme of the sample showing areas A, B, C (C is a sum of A and B) and D used for average reduction rate calculation for in-situ experiments; c) the axial stress distribution evaluated for the initial state of the sample; d) mapping images of the reduction degree in the sample reduced at 650 ^{0}C measured after consecutive steps of the reaction ("stop-and-go" method); selected steps correspond to the Bragg edge patterns in a)).

Figure 2 Bragg edge patterns measured before and after 5 min, 10 min and 50 min of reduction calculated for area A for the sample reduced at 650 ^{0}C (measured using the "stop-and-go" method).

Figure 3 Reduction degrees vs. reduction time averaged over areas A, B and D for sample presented in figure 1 (measured using "stop-and-go" method), reduced at 650 ^{0}C.

Figure 4 Dependence of the reduction rate of NiO-YSZ composite for temperatures reduced at 600 ^{0}C (blue line), 650 ^{0}C (red line), and 800 ^{0}C (green line) (derived for region C of different samples measured in-situ).

Figure 5 Reduction degrees vs. reduction time evaluated for areas A and B for temperatures a) 600 ^{0}C, b) 650 ^{0}C and c) 800 ^{0}C. (for samples measured in-situ).

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