Carbon Tolerance of Ni-Cu and Ni-Cu/YSZ sub- μm sized SOFC Thin Film Model Systems

Thomas Götsch^a, Thomas Schachinger^b, Michael Stöger-Pollach^b, Reinhard Kaindl^c, Simon Penner^{a,*}

^a*Institute of Physical Chemistry, Universität Innsbruck, A-6020 Innsbruck, Austria*

^b*Universitary Service Center for Transmission Electron Microscopy, Vienna University of Technology, A-1040 Vienna, Austria*

^c*Institute for Surface Technologies and Photonics, Joanneum Research — Materials, A-8712 Niklasdorf, Austria*

Abstract

Thin films of YSZ, unsupported Ni-Cu 1:1 alloy phases and YSZ-supported Ni-Cu 1:1 alloy solutions have been reproducibly prepared by magnetron sputter deposition on Si wafers and NaCl(001) single crystal facets at two selected substrate temperatures of 298 K and 873 K. Subsequently, the layer properties of the resulting sub- μm thick thin films as well as the tendency towards carbon deposition following treatment in pure methane at 1073 K has been tested comparatively. Well-crystallized structures of cubic YSZ, cubic NiCu and cubic NiCu/YSZ have been obtained following deposition at 873 K on both substrates. Carbon is deposited on all samples following the trend Ni-Cu (1 : 1) = Ni-Cu (1 : 1)/YSZ > pure YSZ, indicating that at least the 1 : 1 composition of layered Ni-Cu alloy phases is not able to suppress the carbon deposition completely, rendering it unfavorable for usage as anode component in sub- μm sized fuel cells. It is shown that surfaces with a high Cu/Ni ratio prohibit any carbon deposition, however.

Keywords: SOFC anode, carbon deposition, NiCu, YSZ, thin films

1. Introduction

Solid oxide fuel cells (SOFCs), in contrast to other fuel cell systems, use a solid, inorganic material as electrolyte. The latter, in most cases, is yttria-stabilized zirconia. The high operating temperatures of 700 °C to 1000 °C allow for converting also carbon-containing fuels (e.g. methane) internally into water and carbon dioxide.[1] Cost-effective internal reforming then allows the establishment of more simple and cheaper systems and the released heat will additionally accelerate the endothermal methane reforming reaction. Over the years, solution of basic scientific and technological problems was in the focus of a number of both basic and more application-oriented research.[2] One of the most crucial problems of nowadays Ni cermet anodes is connected to the formation of carbon whiskers if they are exposed to hydrocarbon

*Corresponding author: Simon Penner, Innrain 80-82, A-6020 Innsbruck, Austria; Email, simon.penner@uibk.ac.at; Phone, +43 512 507 58003

fuels at high temperatures.[3–5] The ultimate consequences are metal dusting of the Ni-containing anodes, mechanical breakdown and electrode failure.[6] Various strategies have been suggested to overcome this problem.[7] Carbon whiskers on directly oxidizing Ni/YSZ anodes treated with natural fuel could be avoided by decreasing the operating temperature to below 700 °C with at the same time increasing the power density of the cell.[8, 9] Another possibility is to increase the steam-to-hydrocarbon ratio, but this leads to a decreased efficiency factor by fuel dilution. Coke formation can be also reversed by admission of steam, which at lower water partial pressures works better for methane than for higher hydrocarbons. It was shown that carbon binds more strongly at catalysts surfaces at higher temperatures and that even the morphology of the resulting carbon architectures depends on the operating temperatures. Graphite structures are thereby formed in the whole temperature region between 600 °C and 1000 °C, but whiskers are only found at temperatures of around 600 °C.[10, 11] Ni-YSZ SOFCs treated under different gas atmospheres in a range of reaction temperatures showed microstructural degradation at the anode surface and a decreasing conductivity at 750 °C. In contrast, at 650 °C carbon is mainly deposited in the inside of the anode, directly affecting fuel diffusion and the electrochemical reactions on the anode side.[7] It has been also shown that methane decomposition and carbon growth is also an issue on pure oxidic materials by encapsulating the oxide grains with layers of distorted graphite.[12]

One way to study such (electro-)catalytic effects at the metal-oxide (e.g. Ni-YSZ) interface is using model catalyst systems.[13] Representative examples of these materials are either real (embedding of Ni particles in YSZ thin films) or so-called inverse model systems (sub-monolayers of oxides on metal substrates). However, a main obstacle that has to be overcome upon dealing with model systems is the so-called “material’s gap”.[14–16] Industrial catalysts usually represent highly porous materials with a large surface area. A large number of works in the last 20 years have shown the value of model thin film system in closing this material’s gap. They represent structurally and morphologically well-defined systems (and, thus, are very well suited for structural studies), but they can at the same time also be treated under close-to-real catalytic conditions (temperatures between 700 °C and 1200 °C, pressures ≥ 1 bar).[17]

An approach to use such model systems and at the same time control the coking, structural degradation and electrochemical efficiency is to use anode model materials with an eventual suppressed carbon dissolution ability. In that respect, conducting ceramics or metals such as Cu, Ag or Au have been successfully tested for application in SOFC cermet anode systems.[2] However, these materials offer some serious drawbacks, including low conductivity or a decreased sintering stability coupled with a low catalytic activity of Cu, Ag and Au.[2, 18] On the other hand, metals like Ni, Co, Pd or Ru are the better electrocatalysts despite their higher carbon solution propensity.[5, 10] Having said that, bimetallic systems, e.g. Cu in combination with Ni or Co, might be systems with a higher sinter-stability up to 900 °C, a better catalytic activity and being at the same time being less prone to coking and carbon whisker formation compared to the pure metals.[2] Model studies on Au-doped Ni single crystals successfully demonstrated the optimization of

the methane steam reforming reaction.[19] The same is true for Cu-Ni alloys, which are reported to yield suppressed carbon whisker formation upon treatment in methane at 800 °C and a significant increase in power density after 500 hours time-on-stream compared to pure Ni cermet materials.[20] These experimental studies were corroborated by recent ab initio calculations, which showed that copper anodes are much less prone to coking and that step edges on Ni-based anodes suppress carbon formation via efficient blocking of lattice sites.[21] Alloyed systems are also capable of blocking carbon volume diffusion and restrict carbon formation to comparably harmless surface deposits.[4] Furthermore, it has also been shown that such surface carbon impurities can be removed efficiently via steam oxidation by catalytical coatings like CeO₂. [4] As for the Cu-Ni systems, Cu-coated Ni foams might improve the energy density, the stability and the sulfur tolerance of SOFCs in the operating temperature range between 750 °C and 900 °C.[22, 23] A higher electrical conductivity for Ni-Cu/YSZ systems (referenced to conventional Ni/YSZ systems) has been obtained by high-energy ball milling.[24] Further improvements could be achieved by combining bimetallic systems, CeO₂ and yttria-stabilized ZrO₂. Such composite anodes were reported to yield good power performance with and without steam addition for hydrocarbon conversion up to C₆ at 700 °C.[25]

The reliability and efficiency of such SOFCs can in general be improved via reduction of the cell dimension, but in particular via decrease of the electrolyte thickness.[26] Such miniaturized micro-SOFCs, fabricated on the basis of thin film technology, could come as a free-standing membrane, but their cell thickness is still in the μm range.[27, 28] They offer the particular advantages of decreased thermal inactivity and mass transport lengths, which directly yield decreased Ohm-like resistivities and larger electro-catalytic areas due to the nanostructural pattern of thin film surfaces. Using physical vapor deposition techniques, such as magnetron sputtering or pulsed laser deposition, such YSZ electrolyte and entire Ni-YSZ anode systems were prepared. Despite the rough and porous substrates, compact and homogeneous coatings and thin films were obtained at high deposition rates. Temperature treatments in either air or hydrogen did not lead to significant structural changes within the layers. Thin YSZ layers on various anode substrates increased the power density of single cells compared to those prepared via conventional wet impregnation.[27, 29–31]

Despite the efforts made in preparing YSZ and Ni-YSZ thin film systems, a comparative preparation of such systems especially with focus on Ni-Cu model thin films and their reactivity and tolerance towards carbon-containing fuels at typical operating temperatures of SOFCs has not been attempted and reported yet. This is an especial pity, since the μm -thick thin films which are reported in this work will serve as the missing link to real μm -sized entire SOF cells. Hence, we have prepared YSZ, YSZ-free Ni-Cu alloys and Ni-Cu-YSZ alloy/oxide films to study their composition, structure, stability and interfaces and their eventual reactivity towards methane at 800 °C. The resulting methane decomposition and carbon deposition will be in the particular focus of the study. Carbon interdiffusion, delamination and deformation all have a significant influence on the layer stability and hence, crucially affect both the structural integrity of the films and the life span of the model cells. As a proper way to prepare such model thin film systems, magnetron

sputtering is considered, using 8YSZ and metallic Ni-Cu targets. these are accordingly evaporized in an Ar atmosphere and the resulting films deposited on Si wafers and NaCl(001) single crystal facets.

2. Experimental

2.1. Preparation of the Samples

Thin film deposition was undertaken in a modified, industrially compatible sputtering plant (Pfeiffer Vakuum, Germany). Thin films have been sequentially sputter deposited by an unbalanced TORUS cathode from Lesker (Kurt J. Lesker Company Ltd, East Sussex, England) and AJA (AJA International, North Scituate, MA, USA). 3 mm thick Yttrium-stabilized (8 mol%) ZrO_2 (YSZ) and Nickel-Copper (Ni/Cu = 1 : 1) target with 76.2 mm (3 in) diameter, bonded on a copper back plate (Sindlhauser Materials GmbH, Kempten, Germany) have been used. The purity of the targets is 99.9 % and 99.95 %, respectively. As substrates, silicon wafers (100) with native SiO_2 layers were used, which were cleaned with isopropanol and dried with nitrogen prior to deposition. The substrates were fixed on a static, floating potential substrate holding device, kept approximately 10 cm away from the sputtering target. The substrate temperature was held at 873 K and monitored with an electrically insulated K-type thermocouple installed at the backside of the heated substrate holder. YSZ thin film deposition was done by radio-frequency (RF) sputtering at 300 W power and in an 77 % Argon (Ar), 33 % Oxygen (O_2) gas mixture. The deposition pressure was around 5×10^{-2} Pa. Ni-Cu films were deposited after YSZ film deposition by pulsed direct current (DC) sputtering at 200 W power, 80 Hz pulse frequency and 1 s pulse time in pure Ar gas at a pressure of around 4×10^{-2} Pa. The coating thickness was controlled by deposition times estimated from preliminary experiments and cross-checks via AFM and XPS measurements.

2.2. Characterization of the Samples

2.2.1. X-ray Photoelectron Spectroscopy

X-ray photoelectron spectra (XPS) have been acquired using a Thermo Scientific MultiLab 2000, equipped with an Alpha 110 hemispherical channel analyzer, a monochromated X-ray source (emitting Al K_α radiation) and an ion gun for sputter depth profiling by accelerating argon ions to 3 keV. The base pressure of the instrument was in the low 10^{-10} mbar range.

2.2.2. Transmission Electron Microscopy

TEM images and selected area electron diffraction patterns have been recorded employing a ZEISS EM10C, operated at 100 kV. Energy-dispersive X-ray (EDX) spectra and electron energy-loss spectra (EELS) were measured using a FEI Tecnai F20 S-TWIN analytical (high-resolution) transmission electron microscope (200 kV), equipped with an Apollo XLTW SDD X-ray detector as well as a Gatan GIF Tridiem imaging filter.

2.2.3. Atomic Force Microscopy

The surface topology of the samples was measured in intermittent contact mode using a Veeco Dimension 3100 AFM, fitted with Veeco RTESPW cantilevers (with force constants between 20 N m^{-1} and 80 N m^{-1} , as well as resonance frequencies ranging from 256 kHz to 317 kHz).

2.2.4. X-ray Diffractometry

Powder X-ray diffraction (XRD) of the samples was performed using a Bruker D8 Discover diffractometer in Bragg-Brentano geometry. The diffractometer is equipped with a Cu tube, a primary Ge monochromator, and a LYNXEYE detector. Scans were taken in the 2θ range from 10° to 70° with 0.01° steps and a counting time of 2 s per step.

3. Results

Figure 1: Survey XP spectra of (a) YSZ and (b) NiCu, the latter being shown as the outer-most surface spectrum, as well as at a sputtering depth of 2 nm.

X-ray photoelectron spectra of the YSZ and NiCu surfaces are shown in Figure 1 (a) and (b), respectively. For YSZ (a), no impurities are visible, as all the peaks can be attributed to Zr, Y, O, small amounts of Hf (due to the inability to separate Hf from Zr in the production process, all Zr components contain a low fraction of Hf) and carbon. The latter is rather abundant at the surface, with the atomic concentrations of Zr and C being approximately equal. This, however, is limited to the surface, and the carbon is removed by sputtering for a few seconds, leading to the conclusion that it is adventitious carbon resulting from the transport in air. The Zr/Y ratio obtained from the analysis of the corresponding 3d peaks in this spectrum is 5.0, which corresponds to a molar concentration of 9.1 mol% Y_2O_3 . The nickel/copper thin film (b) shows a more intense carbon signal, affecting the whole surface spectrum. In fact, about 10 times more carbon is present than Ni or Cu. Additionally, a pronounced O 1s peak can be discerned. If the specimen is sputtered until a depth of 2 nm from the surface is reached, carbon and oxygen are removed almost fully, and the metallic signals are much more prominent. The Cu/Ni ratio is determined to be 1.1, which is very close to the ideal stoichiometry of 1:1 as found in the target. No impurities were found for this sample either.

In Figure 2, the compositions as a function of the sputtering depth are given for the three types of samples (all prepared at a substrate temperature of 873 K): (a) YSZ, (b) NiCu and (c) a double-layer consisting of NiCu deposited on top of YSZ. In all cases, the x -axis has been normalized to the thin film thickness, which was determined by taking the inflection point from a sigmoidal fit for e.g. the Zr and Si (substrate) signals. In (a), it can be seen that the composition is very homogeneous over the whole thickness of the sample (390 nm). There is a slightly increased concentration of oxygen at the surface which could be due to preferential sputtering of O atoms from the lattice during the depth profiling, and the Zr- and Y-signals drop significantly upon reaching the YSZ/Si interface, whereas the oxygen content increases. This stems from the natural oxide layer present on silicon wafers. The mean of the yttria content taken over all sampled points across the thin film thickness is 9.3(4) mol% Y_2O_3 . As this value agrees perfectly with that obtained for the surface region (see Figure 1), it can be surmised that no segregation of zirconium or yttrium towards the surface takes place.

In the case of the NiCu thin film (Figure 2 (b)), which has a thickness of 180 nm, a significant amount of oxygen is present at the surface, making up almost 60 at% of the total composition. Already at a depth of 2 nm, however, the O content is reduced drastically to about 7 at%. This indicates that the bimetallic thin film is oxidized at its surface (because of the transfer in air), while, in the bulk region of the film, it is still in a reduced state. According to the plot, the surface and surface-near regions are slightly enriched in Cu, with the Ni/Cu ratio being approximately 0.75 in both cases. On the other hand, further inside the film, the Ni concentration is larger than that of the copper. Averaging all data points, the mean Ni/Cu ratio is 0.93(13).

The depth profile of the NiCu/YSZ double layer is shown in Figure 2 (c), again featuring a very high oxygen content at the surface, which rapidly decreases to reveal the existence of a metallic NiCu layer. In

contrast to the pure bimetallic sample, a slight enrichment of nickel at and close to the surface is observed, which is in disagreement with the results found for the NiCu specimen, where a copper segregation towards the surface was found. This could hint at an effect from the underlying YSZ film, which seems to cause a larger fraction of Cu at the interface to be energetically favourable. In total, the Ni/Cu ratio is 0.99(10), so the mean value over the whole film thickness is close to the ideal one. The film thickness of the NiCu layer is 180 nm, the same as for the pure bimetallic film, and the interface between NiCu and YSZ, taken to be the distance in the depth profile between 10 % and 90 % of the copper, nickel and zirconium signals, is 150 nm, which is rather large and could stem from a high surface roughness. The YSZ layer (450 nm) has a mean composition of 9.2(10) mol% Y_2O_3 , which is within the margin of error when compared to the yttria content of the YSZ single layer.

An analysis of the chemical states by means of XPS shows that the surface of YSZ (Figure 3) is fully oxidized, with only Zr(IV) species being present in the Zr 3d spectra. Upon sputtering, small amounts of reduced components, labeled Zr(III) and Zr(II),[32] arise. These stem from the sputtering process itself, as oxygen is prone to be sputtered preferentially, creating suboxidic species in the lattice. The amount of these reduced states being present is relatively constant across the whole film range, with the concentration of fully oxidized zirconium diminishing at the interface to the silicon wafer. The graph in (b) shows an example of the peak fitting applied to the spectra, where the main component is Zr(IV), with the $3d_{5/2}$ peak being located at 182.6 eV. Smaller signals arising from suboxidic and strongly reduced (almost metallic) species are visible at 180.9 eV and 179.3 eV, respectively. Peak fits for the yttrium components were not conducted as the low intensity of the Y 3d peak would lead to erroneous and less reliable results.

In Figure 3 (c), the depth profile of the chemical state of nickel in the NiCu thin film is displayed. Here, it can be observed that the surface looks completely different to the bulk of the film: on the surface, all Ni species are predominantly in the form of nickel(II) hydroxide (resulting from the contact with air), $\text{Ni}(\text{OH})_2$, whereas, upon sputtering to a depth of 2 nm, the amount of this compound is reduced to about 15 %, with about as much NiO being present, and the rest being metallic Ni. The amount of metallic Ni then increases to more than 95 % and remains constant until the interface. Figure 3 (d) shows an exemplary fit for the Ni $2p_{3/2}$ spectrum obtained at a depth of 2 nm. Here, the three components can be distinguished clearly: metallic nickel is found at a binding energy of 852.9 eV (orange),[33] the oxide (red) is located at 854.5 eV,[33] and the hydroxide at 856.1 eV (rendered in blue).[34]

For copper (Figure 3 (e) and (f)), the quantification of the oxidation states, in contrast to Zr and Ni, is not possible because the Cu 2p spectrum for Cu(0) and Cu(I) are very similar, and the distinction is only possible by looking at the shift in the Cu LMM Auger signal. In (e), the Cu 2p region is displayed both for the surface, as well as for a depth of 2 nm. Both spectra have been scaled to the same intensity because at the surface, the peak is very small due to the carbon contaminations already discussed (thus the low signal-to-noise ratio). While, in the bulk, the peaks (which are located at 932.6 eV) are sharp and

no satellite feature is visible around 943 eV, this satellite is very prominent at the surface, indicating the existence of Cu^{2+} , which agrees well with the peak shift (935.3 eV for the $2p_{1/2}$ component), which would even hint at a carbonate or hydroxide species. However, at the surface, there is a distinct shoulder at the lower binding energy side of both the $2p_{3/2}$ and $2p_{1/2}$ peaks, suggesting the existence of a second state with a chemical shift similar to metallic Cu or Cu(I). The Auger peaks in Figure 3 (f) corroborate this: at the surface, the maximum is found at a kinetic energy of 915.7 eV, which is 2 eV lower than what would be expected for CuO. It does, however, agree well with the literature value for a hydroxide.[35] Upon sputtering into the thin film, the peak shifts to 918.5 eV, which is indicative of metallic copper.[36] Copper(I) oxide would yield a peak at 916.8 eV,[37] hence the Auger signal confirms the metallic nature of the thin film already very close beneath the surface.

Figure 4 displays the X-ray photoelectron spectra after heat treatment in methane. In (a), the survey spectra showcase the different amounts of carbon deposited on each sample: for YSZ (lower panel), there is a comparably small amount of C present (about 67 % the amount of Zr and 17 at% in total), whereas there is a significant deposition occurring on NiCu (middle), with carbon making up 97 at% of all species in the sampled region. Indeed, the other peaks — especially the Ni 2p region — are barely visible due to the thick carbon overlayer. For the bilayer (top panel), there is slightly less carbon deposited (88 at%), and the metallic signals are visible considerably better. The C1s regions in (b) highlight the differences in the nature of the deposited carbon species for the different specimens: while for YSZ, the carbon peak is symmetric and composed of sp^3 -hybridized species (with the signals being attributable to C–C bonds (grey), C–O–C (blue) and O–C=O (orange) containing species),[38] for the NiCu-terminated thin films, the peaks are highly asymmetric and shifted to lower binding energies, as would be expected for sp^2 carbon, i.e. graphite.[38, 39]

In Figure 4 (c), a depth profile of the carbon-covered NiCu surface is displayed. It depicts the relative copper and nickel concentrations, showing that there is a strong enrichment of copper on the surface (the Ni/Cu ratio is 0.11), and the average Ni/Cu ratio is 0.23, which are significantly less than the value obtained for the as-grown thin film (Ni/Cu = 0.75). This could be due to another segregation process occurring during the methane treatment. It is, however, also possible that, if the surface is not entirely homogeneous, the Ni-rich parts are coated with a thicker carbon layer due to the high susceptibility of C deposition on nickel, whereas the copper-rich grains are, if at all, only covered by a thinner carbon overlayer. The latter theory would explain why the carbon concentration remains above 95 at% even after etching until a depth of 70 nm is reached, although the metallic signals are observed in the spectra already before etching. According to the inelastic mean free path lengths of electrons with kinetic energies of 554 eV (1.36 nm) and 634 eV (1.50 nm) for Cu $2p_{3/2}$ and Ni $2p_{3/2}$ electrons, respectively, it shouldn't be possible to measure photoelectrons originating from beneath a > 70 nm thick carbon overlayer. The only explanation would be that only grains with Ni/Cu ≈ 0.23 in average, which are only covered by a thin carbon layer, are sampled by this method, whereas those

with a higher Ni/Cu ratio are inaccessible due to the pronounced C deposition.

The thin films that have been deposited on NaCl(001) single crystals were subsequently used for TEM analyses. Figure 5 shows bright field and diffraction data for the YSZ sample in its as-grown state (after treatment in CH₄, the sample remains unchanged; hence, they are not shown here). In the bright field micrograph (a) that was obtained at an area where the film was torn, it can be seen that the specimen consists of small, rounded grains with diameters of around 10 nm. No deposited carbon layers can be witnessed in the micrograph, unlike for the NiCu sample heat-treated in methane (see Figure 6). The corresponding selected area diffraction pattern in (b) reveals the presence of a polycrystalline sample with negligible texturing effects, as well as the existence of either a tetragonal or a cubic phase — which both yield the same rings in the pattern due to having the same lattice spacings, as discussed elsewhere.[40] The assignment of the crystal class can be performed by using a previous study where we investigated YSZ thin films of varying composition that had been deposited using a different sputtering mechanism,[40] wherein the lattice parameter c (corresponding to the height of the unit cell), which is the same for cubic and tetragonal polymorphs, was plotted as a function of the Y₂O₃ content, displaying a discontinuous trend with a recession of the lattice parameter between 8 mol% and 20 mol% of yttria, indicating a phase transition from the tetragonal to the cubic phase. These values are displayed in Figure 5 by red dots, whereas the height of the unit cell for the YSZ thin film prepared in this study, calculated to be 0.516 nm by measuring all rings visible in the pattern (as described in the cited paper), is denoted by a blue square (located at 9.3 mol% Y₂O₃, corresponding to the mean value for the XPS depth profile since the diffraction pattern was obtained in transmission). It can be seen clearly that the lattice parameter is much smaller than for the thin film with 8 mol% Y₂O₃. This would suggest that, even though there is a slightly larger amount of the bigger ion present in the crystal structure, the unit cell volume would be significantly less, which is not possible. Due to this and because of the good collinearity with the lattice parameter of the cubic phases at 20 mol% and 40 mol% yttria, the crystal structure can be assigned to the cubic lattice system in this case. Hence, the spacings found in the pattern are 0.30 nm for the cubic (111) planes, the second-innermost ring at 0.26 nm corresponds to the (200) lattice spacings, and at 0.18 nm, there are the (200) spots of cubic YSZ.[41]

Previously, the phase transition between tetragonal and cubic YSZ thin films was only determined to lie between 8 mol% and 20 mol% Y₂O₃, but now that the 9.3 mol% specimen is found to be cubic, this can be narrowed down significantly: the phase transition must be between 8 mol% and 9.3 mol% yttria, which also explains the apparent discrepancies regarding the determined crystal classes of YSZ samples with stoichiometries in this region found in literature: these samples are so close to the phase boundary that either small deviations in the composition (such as those produced by the sputtering process) or small amounts of contaminations might already stabilize the other structure.

In Figure 6, TEM data for the NiCu thin film after treatment in methane are shown: the bright field image in (a) reveals pronounced carbon depositions that seem to cover the bimetallic grains like a film.

Furthermore, especially in the lower region, carbon filaments or nanotubes can be observed to grow from the crystallites. Figure 6 (b) displays the respective diffraction pattern, which shows that, both, the cubic NiCu phase, as well as graphite are present. The assignment was based on the presence of the NiCu(111) (fcc) ring at 0.21 nm, which coincides with the graphite (100) signal, and the (200) spacings that are found at 0.17 nm.[42] The presence of graphite was confirmed by the (002) spots at 0.34 nm,[43] which exhibit a pronounced ordering. This indicates that at least a portion of the carbon deposits are crystalline, which is to be expected for a nickel-containing alloy. It does, however, show that, also in thin film systems, a 1 : 1 NiCu alloy does not prevent the carbon growth altogether either — the same as for bulk samples.[20] Figure 6 (c) shows EEL spectra recorded across the width of one of the mentioned carbon filaments that was growing on the sample, confirming the filament to be a multi-walled carbon nanotube (with a wall thickness of about 9 nm and total widths of 35 nm). Furthermore, if the π^*/σ^* ratio is taken as a measure, it can be seen that the rim regions, where this ratio is larger (namely up to 0.85, compared to 0.5 in the central region), are more graphitic, which can be explained by the strong sp^2 character of the multi-walled tubes, which resemble graphite layers (for which $\pi^*/\sigma^* \approx 1$).[44]

To assess the local chemical composition, the EDX spectrum image in Figure 7 was recorded, representing the NiCu/YSZ specimen, where, due to the large thickness of this bilayer, an area had to be chosen where the YSZ film was torn away. The spectrum image of the as-grown sample (Figure 7 (a), with the HAADF image of the same spot in (b) and the elemental maps in (c)) reveals that the sample consists of particles with varying Ni/Cu ratios, ranging from predominantly Ni-containing particles, as is found in the upper right corner, to mixed particles that are either Cu-rich (bottom right) or Ni-rich (on the left edge) in composition, and to particles that almost only consist of copper (left). What can be discerned from these images is that the particles consisting of a majority of Cu are less oxidized than their Ni-rich counterparts. This is especially visible in Figure 7 (c) at the bottom right or top left, where there is a clear decrease in oxygen content at the same place where the Cu concentration is highest. The Ni/Cu ratio across the whole image is 0.96, i.e. very close to the composition of the target, and in good agreement with XPS results.

In contrast to the as-grown samples, the specimen exposed to methane at 1073 K features a completely different morphology, as seen in Figure 8. In (a), the complete mapping is shown, whereas the small images in (b) act as a legend as well as to show the distribution of the separate elements, and (c) shows the high-angle annular dark field image of the same region, displaying mass contrast. It can be seen that most of the grains visible are rather inhomogeneous. Besides an oxide shell, which is to be expected for such small, highly reactive particles that have been exposed to air, they seem to resemble Cu-oxide/nickel core-shell particles, with the majority of the nickel being in the center (with a Ni/Cu ratio of about 7 for the particle cores). Additionally, the carbon distribution primarily seems to be focused on the area between the crystallites, although there are some facets in the central region of the image where no carbon seems to have grown at all. This primarily stems from the composition of these particles: whereas, for the faces where there is

carbon growth occurring, the surface-near region has a Ni/Cu ratio of about 3.5 to 5, i.e. is also Ni-enriched compared to the ideal 1 : 1 composition, the areas where there is no carbon deposition have a Ni/Cu ratio of about 0.5 (denoted by small blue arrows in Figure 8 (a)). This suggests that a Cu-enrichment at the surface indeed inhibits the carbon growth, and it is the inhomogeneity of the bimetallic species in the thin film that causes the graphite to be formed.

Regarding the Cu/Ni distribution of the NiCu layer in the NiCu/YSZ sample, it can be summarized that, in the as-grown specimens, it is not entirely homogeneous, with particles ranging from Ni to Cu being present, which increase in size significantly upon treatment in methane (going from about 100 nm to more than 1000 nm in diameter), and change their morphology to a core/shell structure that is more Cu-rich on most of the surfaces. These surfaces with the higher Cu-content also prevent the carbon deposition from the gas phase (CH_4). In order to increase the degree of Cu segregation, a preliminary reductive treatment at high temperature could be employed in order to allow the system to relax into its energetic minimum.[20] These results, however, are in clear contrast to the findings obtained in another work regarding Ni-Cu nanoparticles supported on ZrO_2 ,[45], where it was found that, while copper-enriched facets are preferable at lower temperatures, Ni segregates to the surface at raised temperatures and upon exposition to methane. We could not reproduce this in our thin films, as the EDX spectrum images doubtlessly reveal a Cu-rich shell around a predominantly Ni-containing core after the sample has been heated in a CH_4 environment. This could indicate that the particle size plays a role in the energetics of the diffusion processes, since the crystallites in our thin films are larger than the nanoparticles (100 nm compared to 20 nm).

Additional crystallographic information about the specimens (deposited on Si) was obtained by powder X-ray diffraction (XRD) measurements, the results of which can be seen in Figure 9. The bottom-most diffraction pattern corresponds to the YSZ thin film, and all the signals observed can be attributed to cubic YSZ,[41] marked by the diamond shape in the plot. From the position of the (111) reflex of this structure (29.91°), the lattice parameter can be calculated to be 0.517 nm, which agrees well with the results obtained by SAED (0.516 nm), and which also fits with the determination of a cubic phase. The perfect match between XRD results (Si substrate) and TEM data (NaCl substrate) also indicates that there is no influence of the substrate on the unit cell dimensions. After the specimen has been heated to 1073 K in CH_4 , additional peaks appear in the diffractogram (marked by triangles). These stem from the silicon substrate,[46] which causes the appearance of a very intense peak at about 69° (not shown in the plots) for all samples, and exhibits additional reflexes here. This could be due to sintering of the film, causing the substrate to be exposed (because of holes in the thin film). Furthermore, the YSZ-related peaks are shifted to higher scattering angles with respect to the as-grown sample, which can be explained by a reduction in the size of the unit cell. In fact, the unit cell now has shrunk to $a = 0.510$ nm. No signals from a crystalline carbon species such as graphite are visible, meaning that either the deposited overlayer is too thin to be observed using XRD, or that it is amorphous carbon — which would fit with the observation that

no carbon layers are visible in the TEM bright field images.

The blue diffractograms in Figure 9 were recorded for the bimetallic species. The lower one features two peaks at 43.84° and 51.10° , corresponding to the (111) and (200) lattice planes of cubic NiCu (fcc), respectively (denoted by the squares).[42] Here, the lattice parameter is 0.357 nm. That the signals are attributed only to the alloyed phase with 1 : 1 stoichiometry (NiCu), and not to the almost-pure metals as well, the presence of which could be observed in the EDX spectrum images, is due to the negligibly small differences between the lattice parameters of the two metals (3.597 Å for Cu compared to 3.499 Å for Ni).[47] These cannot be distinguished in the XRD pattern, especially with the existence of additional reflexes from the mixed phases. After treatment in methane, all reflexes stemming from NiCu are blocked by the thick carbonic layer deposited by the methane treatment. The only signals present are from graphite (circles), with the (002) reflex being located at 26.57° , and the (101) planes cause the signal at 44.52° . In general, the signal-to-noise level is very low, suggesting that a large portion of the carbon might be amorphous.

The double-layer system yields both, reflexes for YSZ, as well as for NiCu. The unit cell dimensions of the former can be determined to be 0.521 nm — slightly larger than it was for the YSZ single layer. In fact, if the phase diagram in Figure 5 (c) is drawn to comparison, this value is actually closer to that of the tetragonal species with 8 mol% Y_2O_3 than to the cubic one found for the pure film. Just like the YSZ thin film, the YSZ unit cell in the double layer also shrinks after heating in methane ($a = 0.509$ nm) — to a very similar value as that obtained for the single layer, which would contradict the theory of the YSZ in NiCu/YSZ being tetragonal. However, it could be that, in this instance, the as-deposited film is indeed tetragonal and, due to the already discussed likelihood of the tetragonal/cubic phase boundary being somewhere between 8 mol% and 9.3 mol%, it is possible that a very minor perturbation such as a slightly larger amount of carbon contamination during the sputtering process causing the thin film to transgress the phase boundary and completely change its crystal structure. For the nickel-copper unit cell, the lattice parameter is 0.357 nm, just as for the pure thin film; this indicates that there is no influence of the underlying YSZ layer on the unit cell. This is because the lattice mismatch between the two-dimensional unit cells of the YSZ(001) and NiCu(001) faces is negligibly small (2 %).

In Figure 10, AFM topology images are shown for states before and after heat treatment in CH_4 at 1073 K. In (a), the surface of the YSZ thin film is displayed, which features a rather flat surface, exhibiting a bimodal grain size distribution, that is the surface consists of grains with a diameter of 69(1) nm and is decorated with protrusions of various heights and diameters of 132(2) nm. The RMS surface roughness of this surface is 12.0 nm. Upon treatment with methane (d), the YSZ surface seems to be unchanged, as the same protrusions are found on the surface. Indeed, the surface roughness for the area presented is just 7.6 nm — even lower than for the as-grown film. This most likely is due to the surveyed area not featuring a protrusion as high as for the as-deposited specimen (with the z -height being 65.1 nm instead of 180.7 nm) since the squares of the heights are summed up for this roughness property. The lateral diameter of each

“grain type” is increased by about 10 nm when compared to the as-grown films.

The NiCu surface (b) looks vastly different as it features larger grains (with the center of a Gauss-fit of the histogram at 206(5) nm) and a more homogeneous topology. However, despite the larger grain sizes, the z -span of this image is smaller than for YSZ, with only 97.9 nm. The roughness is comparable to that of YSZ (14.9 nm). Upon heating the sample in methane, the surface topology undergoes a huge alteration: the z extent is increased from 97.9 nm to 5.699 μm due to the carbon deposition (as mentioned earlier). This large height made it difficult to obtain artifact-free micrographs as the large steepnesses caused problems with the tip tracking, even at lower scan speeds. The surface after methane treatment consists of large platelets with the already-mentioned steep edges that seem to stem from the graphite layers stacked on top of each other. This is also reflected in the surface roughness, which now equals 1011.7 nm — an almost hundred-fold increase over the initial state of the surface. No grains of the underlying NiCu thin film are visible anymore, corroborating the results from the XPS analysis, which stated that the surface was completely covered by carbonic depositions. AFM, however, yields an estimate of the thickness of the carbon layers if the heights of the topology images before and after the respective annealing in CH_4 are compared: the height span of the modified surface topology is about 5.6 μm higher than that of the as-grown specimen, indicating that the carbon overlayer generated from contact with the CH_4 molecules at 1073 K is thicker than 5 μm , which is too thick to be measured by sputter depth profiling in an adequate amount of time.

The NiCu/YSZ double-layer, in its as-grown state (c), features a very similar topology to the pure NiCu film — which is explained by the fact that, in both cases, the terminating layer is NiCu. Additionally, the film thicknesses are high enough to prevent any template effects from the underlying YSZ film to be visible at the surface. The grain size (180(3) nm) is actually a bit smaller than for the pure bimetallic sample. The height of the whole image, on the other hand, is approximately 50 % larger, namely 148.4 nm, which might be an effect of the roughness of the YSZ/NiCu interface, causing the top surface to have deeper trenches, even though the general grain structure looks similar. In addition, the RMS surface roughness value of the NiCu/YSZ specimen is the largest among the three as-grown samples: 18.7 nm.

If this sample is exposed to methane at higher temperatures, the height span of the micrograph increases again (to 2.045 μm), just like in the case of the NiCu film. In contrast to the previously discussed sample, however, the general surface looks different as it now features more globular structures instead of the layered platelets. Also, due to the different morphology and the lower height differences, the RMS surface roughness is only 371.9 nm — about a third of that obtained for the NiCu film.

4. Conclusion

In conclusion, we have successfully reported on the sputter deposition of sub- μm sized YSZ, NiCu and NiCu/YSZ layers. Structural and chemical characterizations accordingly show homogeneous layers both in

surface and bulk regions. Carbon is deposited on all samples following methane exposure at 1073 K for 1 h, yielding the trend: Ni-Cu = Ni-Cu/YSZ > pure YSZ. The 1:1 Ni-Cu alloy phase, both free-standing and YSZ-supported, is not able to block the carbon deposition completely. Hence, at least this particular composition of Ni-Cu alloys does not lead to the anticipated increase in carbon tolerance and in turn renders it unfavorable for further use in SOFC anode systems. Nevertheless, according to the EDX spectrum images that showed that facets with an increased Cu concentration did not exhibit carbon deposition, and since pure copper has a very much decreased tendency for carbon formation, shifting the Ni/Cu composition further towards higher Cu contents might offer an opportunity for further improvement. However, the resulting catalytic activity must be assessed separately, since the eventually increased tolerance towards carbon deposition might come at the cost of a decreased catalytic activity.

Acknowledgements

We thank the Austrian Research Promotion Agency (FFG) for financial support within the program “Energieforschung” (eMISSION) under the project “PVD-Mikro-Festoxidbrennstoffzellen” (project number 848825). Furthermore, we acknowledge financial support by the Austrian Science Fund (FWF) via grant F4503-N16.

References

- [1] R. M. Ormerod, Solid oxide fuel cells, *Chem. Soc. Rev.* 32 (1) (2003) 17–28. doi:10.1039/B105764M.
- [2] M. D. Gross, J. M. Vohs, R. J. Gorte, Recent progress in SOFC anodes for direct utilization of hydrocarbons, *J. Mater. Chem.* 17 (30) (2007) 3071. doi:10.1039/B702633A.
- [3] S. McIntosh, R. J. Gorte, Direct Hydrocarbon Solid Oxide Fuel Cells, *Chem. Rev.* 104 (10) (2004) 4845–4866. doi:10.1021/cr020725g.
- [4] T. Kim, G. Liu, M. Boaro, S.-I. Lee, J. M. Vohs, R. J. Gorte, O. H. Al-Madhi, B. O. Dabbousi, A study of carbon formation and prevention in hydrocarbon-fueled SOFC, *J. Power Sources* 155 (2) (2006) 231–238. doi:10.1016/j.jpowsour.2005.05.001.
- [5] M. Toebe, Impact of the structure and reactivity of nickel particles on the catalytic growth of carbon nanofibers, *Catal. Today* 76 (1) (2002) 33–42. doi:10.1016/S0920-5861(02)00209-2.
- [6] C. H. Toh, P. R. Munroe, D. J. Young, K. Foger, High temperature carbon corrosion in solid oxide fuel cells, *Mater. High Temp.* 20 (2) (2014) 129–136. doi:10.1179/mht.2003.016.
- [7] T. Chen, W. G. Wang, H. Miao, T. Li, C. Xu, Evaluation of carbon deposition behavior on the nickel/yttrium-stabilized zirconia anode-supported fuel cell fueled with simulated syngas, *J. Power Sources* 196 (5) (2011) 2461–2468. doi:10.1016/j.jpowsour.2010.11.095.
- [8] Y. Lin, Z. Zhan, J. Liu, S. Barnett, Direct operation of solid oxide fuel cells with methane fuel, *Solid State Ionics* 176 (23–24) (2005) 1827–1835. doi:10.1016/j.ssi.2005.05.008.
- [9] J. Liu, Operation of anode-supported solid oxide fuel cells on methane and natural gas, *Solid State Ionics* 158 (1–2) (2003) 11–16. doi:10.1016/S0167-2738(02)00769-5.

- [10] Baker, R. T. K., J. J. Chludzinski, In-situ electron microscopy studies of the behavior of supported ruthenium particles. 2. Carbon deposition from catalyzed decomposition of acetylene, *J. Phys. Chem.* 90 (20) (1986) 4734–4738. doi:10.1021/j100411a005.
- [11] H. He, J. M. Hill, Carbon deposition on Ni/YSZ composites exposed to humidified methane, *Appl. Catal., A* 317 (2) (2007) 284–292. doi:10.1016/j.apcata.2006.10.040.
- [12] M. Kogler, E.-M. Köck, M. Stöger-Pollach, S. Schwarz, T. Schachinger, B. Klötzer, S. Penner, Distinct carbon growth mechanisms on the components of Ni/YSZ materials, *Mater. Chem. Phys.* 173 (2016) 508–515. doi:10.1016/j.matchemphys.2016.02.046.
- [13] K. Hayek, M. Fuchs, B. Klötzer, W. Reichl, G. Rupprechter, Studies of metal–support interactions with “real” and “inverted” model systems: reactions of CO and small hydrocarbons with hydrogen on noble metals in contact with oxides, *Top. Catal.* 13 (1/2) (2000) 55–66. doi:10.1023/A:1009072519733.
- [14] D. W. Goodman, Model Studies in Catalysis Using Surface Science Probes, *Chem. Rev.* 95 (3) (1995) 523–536. doi:10.1021/cr00035a004.
- [15] G. A. Somorjai, Y. Li, Introduction to surface chemistry and catalysis, 2nd Edition, Wiley, Hoboken, N.J., 2010.
- [16] F. Gao, D. W. Goodman, Model catalysts: simulating the complexities of heterogeneous catalysts, *Annu. Rev. Phys. Chem.* 63 (2012) 265–286. doi:10.1146/annurev-physchem-032511-143722.
- [17] H. Lorenz, C. Rameshan, T. Bielez, N. Memmel, W. Stadlmayr, L. Mayr, Q. Zhao, S. Soisuwan, B. Klötzer, S. Penner, From Oxide-Supported Palladium to Intermetallic Palladium Phases: Consequences for Methanol Steam Reforming, *ChemCatChem* 5 (6) (2013) 1273–1285. doi:10.1002/cctc.201200712.
- [18] S. Jung, C. Lu, H. He, K. Ahn, R. J. Gorte, J. M. Vohs, Influence of composition and Cu impregnation method on the performance of Cu/CeO₂/YSZ SOFC anodes, *J. Power Sources* 154 (1) (2006) 42–50. doi:10.1016/j.jpowsour.2005.04.018.
- [19] F. Besenbacher, Design of a Surface Alloy Catalyst for Steam Reforming, *Science* 279 (5358) (1998) 1913–1915. doi:10.1126/science.279.5358.1913.
- [20] H. Kim, C. Lu, W. L. Worrell, J. M. Vohs, R. J. Gorte, Cu-Ni Cermet Anodes for Direct Oxidation of Methane in Solid-Oxide Fuel Cells, *Journal of The Electrochemical Society* 149 (3) (2002) A247. doi:10.1149/1.1445170.
- [21] N. Galea, D. Knapp, T. Ziegler, Density functional theory studies of methane dissociation on anode catalysts in solid-oxide fuel cells: Suggestions for coke reduction, *J. Catal.* 247 (1) (2007) 20–33. doi:10.1016/j.jcat.2006.12.021.
- [22] Q.-X. Low, W. Huang, X.-Z. Fu, J. Melnik, J.-L. Luo, K. T. Chuang, A. R. Sanger, Copper coated nickel foam as current collector for H₂S-containing syngas solid oxide fuel cells, *Appl. Surf. Sci.* 258 (3) (2011) 1014–1020. doi:10.1016/j.apsusc.2011.07.133.
- [23] X.-Z. Fu, J. Melnik, Q.-X. Low, J.-L. Luo, K. T. Chuang, A. R. Sanger, Q.-M. Yang, Surface modified Ni foam as current collector for syngas solid oxide fuel cells with perovskite anode catalyst, *Int. J. Hydrogen Energy* 35 (20) (2010) 11180–11187. doi:10.1016/j.ijhydene.2010.07.038.
- [24] H. S. Hong, S. Lee, Fabrication and characterization of 900 °C-sintered Ni/Cu/YSZ cermet high temperature electrolysis cathode material prepared by high-energy ball-milling method, *J. Alloys Compd.* 538 (2012) 201–204. doi:10.1016/j.jallcom.2012.06.002.
- [25] H. Kim, S. Park, J. M. Vohs, R. J. Gorte, Direct Oxidation of Liquid Fuels in a Solid Oxide Fuel Cell, *J. Electrochem. Soc.* 148 (7) (2001) A693. doi:10.1149/1.1374216.
- [26] A. Evans, A. Bieberle-Hütter, J. L. Rupp, L. J. Gauckler, Review on microfabricated micro-solid oxide fuel cell membranes, *J. Power Sources* 194 (1) (2009) 119–129. doi:10.1016/j.jpowsour.2009.03.048.
- [27] A. Evans, M. Prestat, R. Tölke, Schlupp, M. V. F., L. J. Gauckler, Y. Safa, T. Hocker, J. Courbat, D. Briand, de Rooij, N. F., D. Courty, Residual Stress and Buckling Patterns of Free-standing Yttria-stabilized-zirconia Membranes Fabricated by Pulsed Laser Deposition, *Fuel Cells* 12 (4) (2012) 614–623. doi:10.1002/fuce.201200028.

- [28] A. Evans, C. Benel, A. J. Darbandi, H. Hahn, J. Martynczuk, L. J. Gauckler, M. Prestat, Integration of Spin-Coated Nanoparticulate-Based $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ Cathodes into Micro-Solid Oxide Fuel Cell Membranes, *Fuel Cells* 13 (3) (2013) 441–444. doi:10.1002/fuce.201300020.
- [29] H. Hidalgo, A.-L. Thomann, T. Lecas, J. Vulliet, K. Wittmann-Teneze, D. Damiani, E. Millon, P. Brault, Optimization of DC Reactive Magnetron Sputtering Deposition Process for Efficient YSZ Electrolyte Thin Film SOFC, *Fuel Cells* 13 (2) (2013) 279–288. doi:10.1002/fuce.201200125.
- [30] R. Nédélec, S. Uhlenbruck, D. Sebold, V. Haanappel, H.-P. Buchkremer, D. Stöver, Dense yttria-stabilised zirconia electrolyte layers for SOFC by reactive magnetron sputtering, *J. Power Sources* 205 (2012) 157–163. doi:10.1016/j.jpowsour.2012.01.054.
- [31] A. A. Solovyev, N. S. Sochugov, S. V. Rabotkin, A. V. Shipilova, I. V. Ionov, A. N. Kovalchuk, A. O. Borduleva, Application of PVD methods to solid oxide fuel cells, *Appl. Surf. Sci.* 310 (2014) 272–277. doi:10.1016/j.apsusc.2014.03.163.
- [32] Yoshitaka Nishino, A. R. Krauss, Yuping Lin, D. M. Gruen, Initial oxidation of zirconium and Zircaloy-2 with oxygen and water vapor at room temperature, *J. Nucl. Mater.* 228 (3) (1996) 346–353. doi:10.1016/0022-3115(95)00194-8.
- [33] K. S. Kim, N. Winograd, X-ray photoelectron spectroscopic studies of nickel-oxygen surfaces using oxygen and argon ion-bombardment, *Surf. Sci.* 43 (2) (1974) 625–643. doi:10.1016/0039-6028(74)90281-7.
- [34] A. N. Mansour, Characterization of $\beta\text{-Ni}(\text{OH})_2$ by XPS, *Surf. Sci. Spectra* 3 (3) (1994) 239. doi:10.1116/1.1247752.
- [35] N. S. McIntyre, Chemical information from XPS—applications to the analysis of electrode surfaces, *J. Vac. Sci. Technol.* 18 (3) (1981) 714. doi:10.1116/1.570934.
- [36] C. Battistoni, G. Mattogno, E. Paparazzo, L. Naldini, An XPS and Auger study of some polynuclear copper compounds, *Inorg. Chim. Acta* 102 (1) (1985) 1–3. doi:10.1016/S0020-1693(00)89066-0.
- [37] J. P. Tobin, W. Hirschwald, J. Cunningham, XPS and XAES studies of transient enhancement of Cu^1 at CuO surfaces during vacuum outgassing, *Appl. Surf. Sci.* 16 (3-4) (1983) 441–452. doi:10.1016/0378-5963(83)90085-5.
- [38] Thermo Fisher Scientific Inc., XPS Knowledge Base: Carbon (2016).
URL <http://xpssimplified.com/elements/carbon.php>
- [39] G. Johansson, J. Hedman, A. Berndtsson, M. Klasson, R. Nilsson, Calibration of electron spectra, *J. Electron Spectrosc. Relat. Phenom.* 2 (3) (1973) 295–317. doi:10.1016/0368-2048(73)80022-2.
- [40] T. Götsch, W. Wallisch, M. Stöger-Pollach, B. Klötzer, S. Penner, From zirconia to yttria: Sampling the YSZ phase diagram using sputter-deposited thin films, *AIP Adv.* 6 (2) (2016) 025119. doi:10.1063/1.4942818.
- [41] H. Horiuchi, A. J. Schultz, Leung, P. C. W., J. M. Williams, Time-of-flight neutron diffraction study of a single crystal of yttria-stabilized zirconia, $\text{Zr}(\text{Y})\text{O}_{1.862}$, at high temperature and in an applied electrical field, *Acta Crystallogr., Sect. B: Struct. Sci.* 40 (4) (1984) 367–372. doi:10.1107/S0108768184002329.
- [42] E. Lugscheider, H. Reimann, Das Dreistoffsystem Nickel-Kupfer-Bor, *Monatsh. Chem.* 108 (5) (1977) 1005–1010. doi:10.1007/BF00897680.
- [43] P. Trucano, R. Chen, Structure of graphite by neutron diffraction, *Nature* 258 (5531) (1975) 136–137. doi:10.1038/258136a0.
- [44] P. Ewels, T. Sikora, V. Serin, C. P. Ewels, L. Lajaunie, A Complete Overhaul of the Electron Energy-Loss Spectroscopy and X-Ray Absorption Spectroscopy Database: eelsdb.eu, *Microsc. Microanal.* 22 (3) (2016) 717–724. doi:10.1017/S1431927616000179.
- [45] A. Wolfbeisser, G. Kovács, S. M. Kozlov, K. Föttinger, J. Bernardi, B. Klötzer, K. M. Neyman, G. Rupprechter, Surface composition changes of CuNi-ZrO_2 during methane decomposition: An operando NAP-XPS and density functional study, *Catal. Today* doi:10.1016/j.cattod.2016.04.022.
- [46] W. L. Bond, W. Kaiser, Interstitial versus substitutional oxygen in silicon, *J. Phys. Chem. Solids* 16 (1-2) (1960) 44–45. doi:10.1016/0022-3697(60)90069-X.

- [47] W. P. Davey, Precision Measurements of the Lattice Constants of Twelve Common Metals, *Phys. Rev.* 25 (6) (1925) 753–761. doi:10.1103/PhysRev.25.753.

Figure 2: XPS depth profiling results for (a) YSZ, (b) NiCu and (c) NiCu/YSZ thin films. The x -axis has been scaled to the film thickness.

Figure 3: Chemical state depth profiles, as obtained by XPS, for YSZ (a, b) and NiCu (c-f) thin films.

Figure 4: (a) Survey XP spectra of the three sample types after exposure to CH_4 at 1073 K (with the C1s peak highlighted) and the respective C 1s regions (b). (c) shows the Cu and Ni concentrations as a function of the sputter depth for the NiCu thin film.

Figure 5: TEM bright field image (a) and selected area electron diffraction pattern (b) of the YSZ thin film. (c) shows the lattice parameter c obtained from the diffraction pattern (blue square), compared to those of similar thin films, taken from [40] (red dots).

Figure 6: (a) Bright field image showing the strong carbon depositions on the NiCu sample after heating in methane, which is proven to be graphitic by the electron diffraction pattern in (b). In (c), C-K edges of various points along the diameter of the the carbon nanotube in the HAADF-image (inset) are displayed.

Figure 7: EDX spectrum image (a) and HAADF image (b) of the NiCu/YSZ thin film in its as-grown state. (c) shows the elemental maps. All scale bars are 200 nm.

Figure 8: (a-b) EDX spectrum image of a fringe region of the NiCu/YSZ thin film, revealing Ni/Cu Core-Shell particles that are partially oxidized. (c) shows the respective HAADF micrograph. All scale bars are 2 μm .

Figure 9: X-ray powder diffractograms for the YSZ, NiCu and NiCu/YSZ samples, deposited on Si wafers, before and after treatment in methane at 1073 K.

Figure 10: AFM topology images (obtained in intermittent-contact mode) for YSZ (a,d), NiCu (b,e) and NiCu/YSZ (c,f) before (upper row) and after methane treatment (lower row). All image dimensions are $5 \mu\text{m} \times 5 \mu\text{m}$, and the heights are given in the respective images.