A cermet (ceramic metal composite) of Nickel and Yttria stabilized Zirconia (YSZ) is the most commonly used fuel electrode for Solid Oxide Fuel Cells (SOFC). The properties of such cermets depend strongly on their microstructure. Several Ni/YSZ cermet samples with different Ni content and Ni and 8YSZ grain size have been prepared. The thermal expansion coefficient (TEC) of these samples was measured in air respectively hydrogen and shows a strong dependence on grain size ratio. The kinetic of the oxidation/reduction of these samples was investigated. The oxidation of the cermet is faster than the oxidation of pure NiO and the reduction consists of 2 steps whereas the last step is splitted into 2 concurrent processes.

1 Introduction

SOFCs which convert chemical energy directly into electrical are due to their high efficiency a promising alternative to conventional energy producing techniques. The electrolyte which usually consists of 8YSZ transports oxygen ions to the anode where the fuel (H₂ or CH₄) is electrochemically oxidized. Most SOFC single cells have a homogeneous single layer Ni/8YSZ anode. However, these cells show a high degradation due to a agglomeration of Ni grains during long term operation [1]. This degradation could be prevented by a multilayer anode whose diverse layers differ in their microstructure to fulfill the locally different requirements for SOFC anodes (fig. 1).

Figure 1: Scheme of a multilayer anode

The first layer which is adjacent to the electrolyte should consist of small Ni and 8YSZ grains to provide a great electrochemical active surface. The TEC should be close to that of the electrolyte. The last layer which is in contact with the electrical interconnector should have a
high electronic conductivity and high porosity for gas diffusion. Therefore the content of Ni and the Ni grain size should increase from first to last layer and thus increasing the electronic conductivity, TEC and the porosity. The 8YSZ content should simultaneously decrease.

Because the single cells have to be sintered in air, NiO is used for cermet preparation and reduced not before operation. The reduction of NiO causes a drastic drop in volume and therefore influences the microstructure and the properties of the cermet.

The investigations described in this paper are the first step for the development of a multilayer cermet anode for SOFCs.

2 Experimental

The cermet samples were prepared by mixing 65-85 mol% NiO powder with 8YSZ powder and sintering them in air at 1300°C for 5 hours. The grain size was 0.5-8 µm. Powders with different monomodal grain size distributions were obtained by rotary ball milling.

The TEC between 200 and 1000°C was measured in a Netzsch 402C dilatometer by heating the samples up to 1100°C and holding the temperature for 5 hours. Air and 6% H₂ in N₂ (100 ml/min) was used as atmosphere, respectively. The kinetic of reduction/oxidation was investigated by means of thermogravimetry in a mass balance (Netzsch TG 439). The samples were heated up to 1000°C with various heating rates (2-10 K/min) and 50ml/min O₂ respectively 6% H₂ in N₂. The total porosity of the samples was determined geometrically and in the open porosity was additionally measured in a pygnometer.

3 Results and Discussion

The total porosity of all NiO/8YSZ samples is between 4 and 27% and increases during reduction by a factor of 1.3-1.5 hence resulting in porosity of 26-46%. The quota of open porosity is 40% in the oxidized state and 80% in the reduced state. The porosity increases as the Ni content and the grain size ratio between Ni and 8YSZ increases. This is due to the volume drop of 40% during reduction of NiO.

As can be see in fig. 1a the TEC of the cermet rises by increasing the content of NiO. This effect can be expected because the TEC of pure NiO (14·10⁻⁶ K⁻¹) is higher than that of 8YSZ (11·10⁻⁶ K⁻¹). In addition, the measurements show that the TEC depends on the grain size ratio, too. The bigger the NiO particles are in comparison to the 8YSZ particles, the smaller is the TEC of the cermet. But if the grain size ratio exceeds a certain threshold the TEC increases again (fig. 1b). This effect is independent of the absolute NiO content. These results can be interpreted that the ceramic matrix is stabilizing the cermet and thus determines the overall TEC. The NiO particles can move elastically within the cermet as long as they are small enough. At the minimum of the TEC the cermet has an optimal package configuration which depends on particle shapes and sizes. Elomari et al. reported similar results for the TEC of Al/SiO₂ cermets [2]. The measured data were compared with 2 theoretical curves obtained from the models of Thomas [3] and Schapery [4] who tried to calculate the TEC of
composites. But both models don't incorporate the grain size what explains the disagreement between experiment and model.

The reduced samples show similar behaviour, i.e. the TEC increases with increasing Ni content. But a comparison between oxidized and reduced samples of the same composition (table 1) indicates that not in any case the TEC of the reduced sample is higher than that of the oxidized one as it could be expected (TEC\textsubscript{Ni} =18·10^{-6} K\textsuperscript{-1}). This fact enhances the role of 8YSZ as stabilizing matrix because the matrix remains stable during reduction so that in the reduced state Ni can expand/shrink without influencing the TEC of the whole cermet. But a clear connection between grain size and TEC like in the oxidized state is not visible. This could be due to the fact that 8YSZ forms a stable matrix and cannot be treated any longer as individual grains with a certain grain size.

![Figure 2: TEC of a NiO/8YSZ cermet: a) different NiO contents, b) TEC as a function of grain size ratio](image)

Table 1: TEC (in 10^{-6} K\textsuperscript{-1}) of different samples in oxidized and reduced state.

<table>
<thead>
<tr>
<th>Sample</th>
<th>NiO content</th>
<th>NiO grain size</th>
<th>8YSZ grain size</th>
<th>oxidized</th>
<th>reduced</th>
</tr>
</thead>
<tbody>
<tr>
<td>000000</td>
<td>65 mol%</td>
<td>0.5 µm</td>
<td>0.5 µm</td>
<td>12.5</td>
<td>12.7</td>
</tr>
<tr>
<td>101210</td>
<td>75 mol%</td>
<td>0.8 µm</td>
<td>1 µm</td>
<td>12.7</td>
<td>11.7</td>
</tr>
<tr>
<td>201611</td>
<td>85 mol%</td>
<td>10 µm</td>
<td>1 µm</td>
<td>12.9</td>
<td>12.4</td>
</tr>
</tbody>
</table>

As reference measurements the oxidation and reduction kinetic of pure Ni and NiO powder, respectively, was investigated. Comparison of the theoretical and measured mass loss during oxidation shows that pure Ni is not totally oxidized during heating-up even with a heating rate of only 2K/min. Whereas Ni within a cermet can be totally oxidized. These results are in accordance with literature [5] where the oxidation of Ni is described as diffusion controlled and thus slowly and it is mentioned that the addition of other materials accelerates the Ni oxidation. The reduction of pure NiO is completed at 650°C and indicates 2 single peaks at 350°C and 510°C. When a cermet is reduced the peaks shifts to 410°C and 650°C, respectively (fig. 3a). Drescher et al. [6] investigated the reduction of Ni/8YSZ cermets by analyzing the gas by mass spectroscopy and reported similar results. Furthermore it can be seen that the total mass loss rises with increasing heating rate and is equal or higher than the theoretical mass loss (fig. 3b). This effect can also be seen for pure NiO but is more distinct for the cermet. An experiment only with 8YSZ showed that 8YSZ doesn’t react with H\textsubscript{2} nor does it adsorb enough H\textsubscript{2} to explain the different mass losses. This means that the reduction of
NiO consists of at least 2 steps whereas the last step consists of 2 concurrent processes with different activation energies.

4 Conclusions

It was shown that the TEC of a NiO/8YSZ cermet not only depends on the NiO content but also on the grain size ratio of the 2 components. If the cermet has an optimal package configuration the TEC is lower than theoretically calculated value and shifts towards the TEC of the ceramic. In general, it cannot be said that the TEC of the cermet increases after reduction of NiO to Ni. The 8YSZ matrix can play a stabilizing role so that the TEC of the resulting cermet can be lower than that of the oxidized sample.

The investigation of the oxidation/reduction kinetic revealed that the addition of 8YSZ to Ni accelerates the oxidation and the reduction process consists of at least 2 steps. The last step of the reduction is splitted into 2 concurrent processes so that the total mass loss depends on the heating rate because of the different activation energies of the 2 processes. The physical nature of theses processes has yet not been identified.

5 References