Interfacial properties and structure stability of Ni/Y$_2$ O$_3$-ZrO$_2$-TiO$_2$ cermet anodes for solid oxide fuel cells

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Ceramics of the ternary system Y$_2$O$_3$-ZrO$_2$-TiO$_2$ (YZT) and Ni/YZT cermets are evaluated in terms of application as anode electrodes in a Solid Oxide Fuel Cell. Wetting experiments in liquid Ni/YZT systems show that the increase of TiO$_2$ content in the ceramic phase improves the bond strength at the metal ceramic interface, due to the reduction of the interfacial energy. Ni(40 vol%)/YZT cermets are exposed at 1000°C for up to 1000 h in reducing atmosphere and exhibit an improved long term stability regarding to the electrical conductivity and the microstructure compared to the "state of the art" Ni/8YSZ (yttria(8 mol%)-stabilized zirconia) cermet. This is explained by the enhanced adherence at the Ni/ceramic interface, which suppresses the agglomeration rate of the Ni particles. The improvement of the interfacial properties diminishes the TEC values of the Ni/YZT cermets constraining the thermal expansion mismatch between the cermet anode and the 8YSZ electrolyte in the SOFCs. © *2005 Springer Science + Business Media, Inc.*

1. Introduction

Nickel and yttria (8 mol%)-stabilized zirconia (8YSZ) cermets are the state of the art anodes in the solid oxide fuel cell (SOFC) technology. Disadvantages of the Ni/8YSZ cermet anode are its sulfur intolerance, when natural gas is used as fuel, and the long term degradation of their catalytic activity [1] caused by the agglomeration of Ni-particles at the working temperature between 900 and 1000°C.

Since Ni particles are high surface area and high surface energy solids, there will be always a thermodynamic driving force to decrease the total free energy by minimizing the surface area. Hence, the restructuring behavior of the anode cermet depends on the wetting properties between Ni and 8YSZ. A better adherence of the metal/ceramic interface is expected to reduce the sintering effect of the Ni particles.

Improvement of bonding between Ni metal and 8YSZ ceramic demands the decrease of the interfacial energy values. This can be achieved through modification of the interface by adding interfacial active compounds.

In order to improve the performance of the cermet anode in a SOFC the use of ceramics containing titania is proposed. Because of the mixed ionic-electronic conducting properties of Y$_2$O$_3$-ZrO$_2$-TiO$_2$ (YZT) ceramics [2–4], resulting from the additional electronic conductivity due to the Ti^{4+} $\rightarrow$ Ti^{3+} valence change

under reducing conditions, it is expected that the electrocatalytic reaction would be enhanced due to a more widespread reaction zone [5, 7]. Furthermore in earlier work it was observed that 8YSZ ceramics containing 5 and 10 mol% TiO$_2$ tend to reduce the values of the linear thermal expansion coefficient (TEC) in the temperature range 25–1000°C as well as to enhance the structural stability of the Ni cermets [6, 7].

The aim of this work is to study the interfacial properties in various Ni/YZT systems and their influence on TEC as well as the stability of the cermets through measurement of their electrical conductivity after annealing in reducing atmosphere and long term conditions.

2. Experimental
2.1. Powder preparation
Ceramic powders of 8YSZ and 8YSZ-TiO$_2$ are synthesized by the method of "spray drying" of aqueous nitrate solutions as described in detail elsewhere [8]. The stock solution containing Y^{3+} (15 mol%) and Zr^{4+} (85 mol%) leads to a ceramic with composition Y$_{0.148}$Zr$_{0.852}$O$_{2-x}$ (8YSZ). The mixed oxides resulting from the admixture of 5 and 10 mol% TiO$_2$ have a nominal composition of Y$_{0.141}$Zr$_{0.809}$T$_{0.05}$O$_{2-x}$ (8YSZ5T) and Y$_{0.131}$Zr$_{0.767}$Ti$_{0.10}$O$_{2-x}$ (8YSZ10T).

The YZT powders with different yttria and titania content are synthesized by co-precipitation according
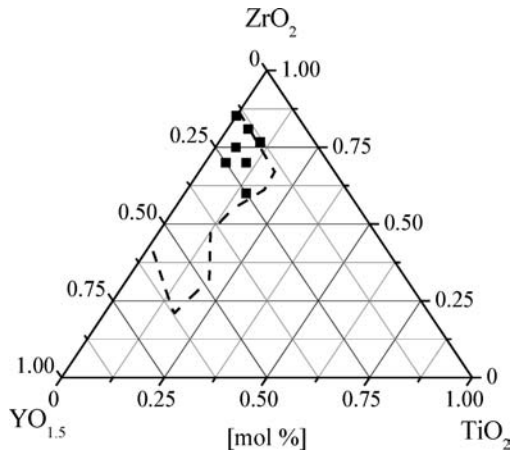
Figure 1 Selected compositions (■) in the ternary phase diagram of $YO_{1.5}$-ZrO_2-TiO_2 at 1500°C [10] (the dashed line indicates the phase field for the cubic fluorite structure).

to the detailed description in [9] with nominal compositions $Y_{0.20}Z_{0.75}Ti_{0.05}O_{2-x}$ (10YSZ5T), $Y_{0.20}Zr_{0.70}Ti_{0.10}O_{2-x}$ (10YSZ10T), $Y_{0.25}Zr_{0.70}Ti_{0.05}O_{2-x}$ (12.5YSZ5T) and $Y_{0.25}Zr_{0.60}Ti_{0.15}O_{2-x}$ (12.5YSZ15T).

Fig. 1 shows the ternary phase diagram of $YO_{1.5}$-ZrO_2-TiO_2 at 1500°C [10]. The mixed oxide compositions chosen are in the limit or inside the phase field for cubic fluorite structure, as indicated by the dashed line and experimentally confirmed by X-ray diffraction analysis of the powders annealed at 1400°C for 5 h.

Parts of the ceramic powders are mixed with the appropriate amounts of NiO (J.T. Baker, >99%) to achieve Ni contents of 30, 40 and 45 vol% after reduction. All mixtures are wet milled with ethanol in centrifugal ball mill for 120 h for homogenization and reduction of the mean grain size.

2.2. Sample preparation

For the examination of the interfacial properties as well as for the thermal expansion and electrical conductivity measurements, disks of 15 mm in diameter and 2 mm in thickness as well as rectangular bars $3 \times 3 \times 25$ mm, respectively, are uniaxially pressed and sintered at 1300°C for 5 h. The density of the samples after sintering is at least 95% of theoretical density. The specimens that contain NiO are sintered at 1300°C for 5 h and subsequently reduced in flowing Ar/4%H_2 atmosphere at 900°C for 5 h. After the reduction of NiO the cermets have a porosity of 15–20%.

All measurements are carried out in flowing Ar/4%H_2 atmosphere. Under these conditions, the partial pressure of oxygen lies between 7×10^{-20} and 16×10^{-20} bar, due to moisture presence (200–300 ppm).

3. Results and discussion

3.1. Interfacial properties in Ni/YZT systems

The interfacial properties are examined using the sessile drop technique. For non-reactive liquid metal/ceramic systems in thermodynamic equilibrium the Young equation holds:

$$\gamma_{SL} = \gamma_{SV} - \gamma_{LV} \cos \theta \qquad (1)$$

TABLE I Surface energy of oxides, γ_{SV}, and liquid nickel, γ_{LV}, as well as contact angle, θ, in Ni/oxide systems at 1500°C [17]

Oxide	γ_{SV} (J/m²)	θ (deg)
Al_2O_3	1.169[1]	119
BeO	1.763[2]	148
MgO	1.756[2]	142
CaO	1.524[2]	139
$MgAl_2O_4$	1.977[2]	156
ThO_2	1.136[1]	133
UO_2	0.894[1]	112
YSZ	1.168[1]	117
TiO_2	0.504[2]	105
Surface Energy of Ni at 1500°C, $\gamma_{LV} = 1.741$ J/m²		

[1]Measured values with uncertainty of ±15–20% [12–15].
[2]Calculated average values [16].

where γ_{LV} and γ_{SV} are the surface energies of the liquid and the solid phase, respectively, γ_{SL} is the interfacial energy of the liquid/solid and θ is the contact angle. Wetting behavior between a liquid metal and a ceramic allows to conclude about the expected interfacial properties in solid metal/ceramic system, taking into account that surface and interfacial energies follow approximately linear temperature functions and $\gamma_{\text{solid metal}} \approx 1.1 \gamma_{\text{liquid metal}}$ [11].

In order to calculate the interfacial energy using Equation 1, the values of the contact angle and the surface energies of the phases are required. For liquid metal/oxide systems the contact angle and the surface energy of the liquid metal can be determined from wetting experiments [12]. The surface energy value of the oxide is difficult to be determined and a combination of experimental methods (e.g. multiphase equilibration technique) is required [12–15], thus most of the existing data are derived from theoretical considerations [16].

Table I includes literature data concerning the surface energy for different oxides and liquid nickel as well as the measured contact angle values (mean values) in the liquid nickel/oxide systems at 1500°C. All systems taken into consideration are non-wetted ($\theta > 90°$) and non-reactive. The limited solubility of the oxides in the liquid metal, especially of oxygen as interfacial active element, does not influence the wetting conditions.

The interfacial energy values, γ_{SL}, of the systems examined can be calculated by Equation 1 using the data γ_{LV}, γ_{SV} and θ given in Table I. Fig. 2 illustrates the interfacial energy in the liquid Ni/oxide systems at 1500°C in dependence of $\cos \theta$. These values approximately follow a linear relationship

$$\gamma_{SL} = -3.691 \cos \theta + 0.117 \qquad (2)$$

Combination of Equations 1 and 2 gives

$$\gamma_{SV} = -1.950 \cos \theta + 0.117 \qquad (3)$$

Equation 3 enables the calculation of the surface energy of an oxide at 1500°C after wetting experiment in contact with liquid Ni.

Wettability experiments were carried out in the systems of the mixed oxides (YZT) as ceramic substrates and Ni ingots (~0.3 g) of a purity 99.99 wt% (Alfa Products). The sessile drop experiments are performed
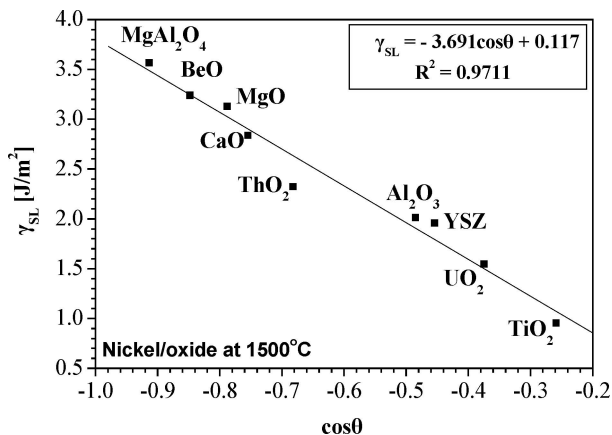
Figure 2 Interfacial energy, γ_{SL}. vs. $\cos\theta$ of various oxides in contact with liquid Ni at 1500°C in Ar/4%H$_2$ atmosphere.

TABLE II Contact angle, θ, interfacial energy, γ_{SL}, in Ni/mixed oxide systems and surface energy, γ_{SV}, of the mixed oxides at 1500°C in Ar/4% H$_2$

Systems	θ (deg)	γ_{SL} (J/m^2)	$\gamma_{SV,oxide}$ (J/m^2)
Ni/8YSZ	117.0	1.793	1.002
Ni/8YSZ5T	107.1	1.202	0.690
Ni/10YSZ5T	112.1	1.506	0.851
Ni/12.5YSZ5T	113.1	1.559	0.879
Ni/8YSZ10T	105.7	1.116	0.645
Ni/10YSZ10T	110.5	1.410	0.800
Ni/12.5YSZ15T	104.6	1.047	0.609

in a horizontal high frequency induction furnace coupled with a molybdenum susceptor in flowing Ar/4%H$_2$ atmosphere at 1500°C. Optical windows permit the in-situ observation of the sessile drop in a monitor as well as the measurement of the temperature using an optical pyrometer (± 10°C). Each experiment lasted about 20 min. The established equilibrium contact angle does not change during the experiment. Table II shows the measured contact angle values as well as the corresponding interfacial energy (Equation 2) and the oxide surface energy (Equation 3) values in the tested systems.

The results (Table II) show that the increase of TiO$_2$ content in the mixed oxides improves wetting by decreasing the contact angle. On the contrary, for the same TiO$_2$ content, the presence of higher Y$_2$O$_3$ concentra-

tion in the mixed oxides reduces wetting by increasing the contact angle. Since the measured contact angle values are between the values for liquid Ni/TiO$_2$ ($\theta = 105$°) and liquid Ni/8YSZ ($\theta = 117$°) the calculated values (Equations 2 and 3) for the interfacial and surface energy of the mixed oxides are in the same range between the two systems. Extrapolating the results regarding the interfacial properties of the liquid/solid state to the solid/solid state, it is expected that the presence of TiO$_2$ in the mixed oxides will benefit the interfacial bonding between solid Ni and the mixed oxides in a cermet anode electrode of a SOFC at working temperature.

Post examination by SEM—EDAX on cross-sections of the samples (Fig. 3) after wetting experiments shows no interaction at the metal/ceramic interface, since the interface exhibits no irregularities and the line scanning has a sharp transition from metallic to ceramic phase. This is in accordance with wettability results performed between liquid Ni and TiO$_2$ coated 8YSZ ceramic [18].
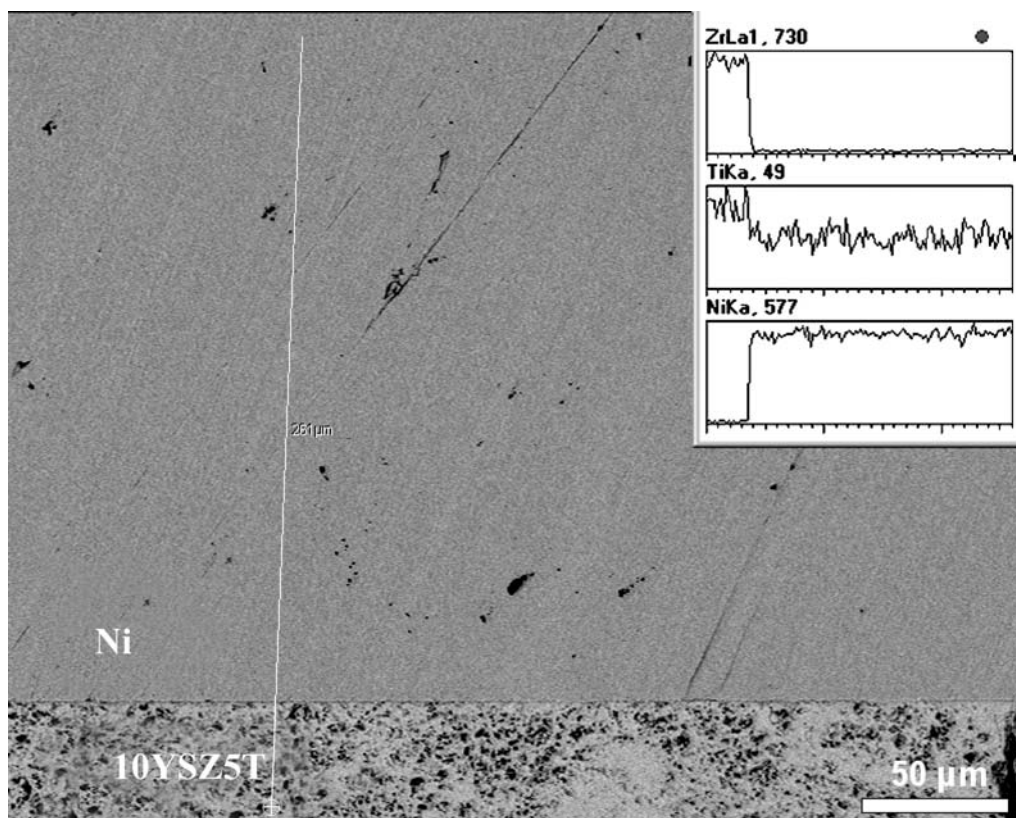

Figure 3 Cross section image and line scan of the Ni/10YSZ5T interface after sessile drop experiment at 1500°C in Ar/4%H$_2$ atmosphere.
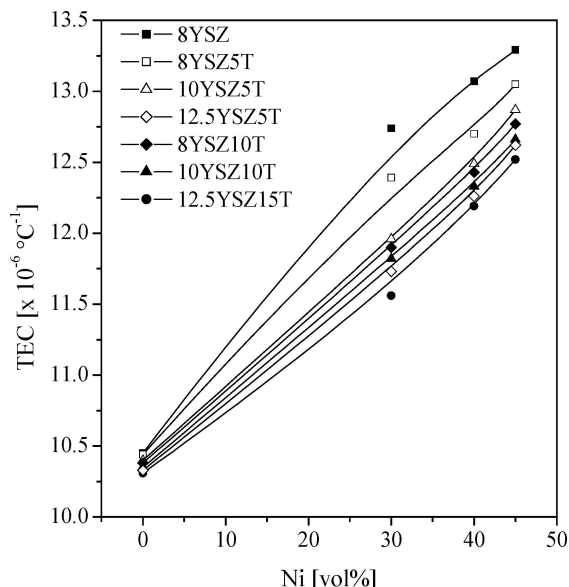
Figure 4 Linear thermal expansion coefficient (TEC) values for the different Ni/mixed oxide cermets measured in the temperature range 25–1000°C in Ar/4%H₂ atmosphere.

3.2. Thermal expansion of YZT and Ni/YZT cermets

The thermal expansion coefficients (TECs) are measured using a push-rod dilatometer (Netzsch) in the temperature range between 25 and 1000°C under a flowing Ar/4%H₂ atmosphere for the YZT ceramics and Ni/YZT cermets with 30, 40 and 45 vol% Ni. The results are illustrated in Fig. 4 and compared with the corresponding values for 8YSZ and Ni/8YSZ (5 and 10 mol% TiO₂) cermets [7].

The presence of TiO₂ ($\alpha = 8 \times 10^{-6}$ °C⁻¹) and Y₂O₃ ($\alpha = 8.6 \times 10^{-6}$ °C⁻¹) [19] in the mixed oxides leads to a slight decrease of the TEC values compared to the "state of the art" YSZ ($\alpha = 10.5 \times 10^{-6}$°C⁻¹) ceramic. Significant deviations are observed in the cermet materials with the same Ni content where the increase of TiO₂ leads to a reduction of the TEC values. According to the wettability results, the presence of TiO₂ in the ceramic phase improves the interfacial bonding between solid Ni and the ceramic phase. The enhanced adherence at the interface restrains the movement of the Ni particles on the plane of contact with the ceramic, resulting in smaller vibration modes at the particle interface, suppressing in this way its expansion and leading to lower TEC-values. The achieved TEC values of the Ni/YZT cermets are beneficial in terms of their application in SOFCs due to constrained thermal expansion mismatch between the cermet anode and the YSZ electrolyte.

3.3. Electrical conductivity and microstructure stability of Ni/YZT cermets

Electrical conductivity is measured between room temperature and 900°C in Ar/4%H₂ atmosphere using a four-probe DC technique with Ag wires wrapped around the samples. Current and voltage are measured with a multimeter (Keithley) and automatically recorded using the Test Point software package.
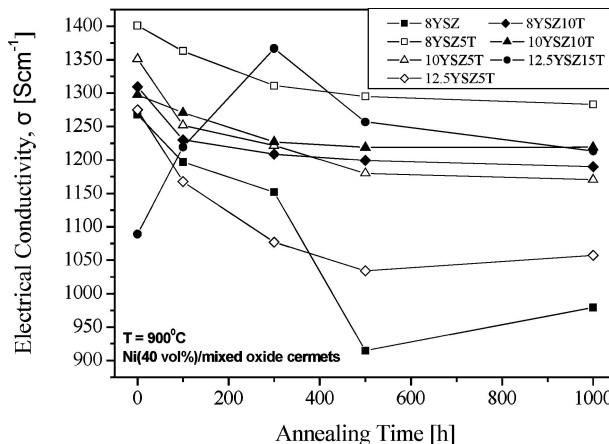

Figure 5 Electrical conductivity at 900°C of Ni(40 vol%)/mixed oxide cermets in dependence of the annealing time at 1000°C in Ar/4%H₂ atmosphere.

The temperature dependence of electrical conductivity of the cermets exhibits metallic character, with values that depend on the Ni content. Samples with 30 vol% Ni are in the percolation limit of the S-type curve of electrical conductivity for cermets with 15 to 20% porosity [20] and therefore reach lower conductivity values.

The long term stability of electrical conductivity of the Ni(40 vol%)/YZT cermets is examined after exposure at 1000°C in Ar/4%H₂ atmosphere for 1000 h. At fixed time intervals the annealing is interrupted and the sample's electrical conductivity is measured in the temperature range of 25–900°C. Fig. 5 illustrates the electrical conductivity of the Ni(40 vol%)/YZT cermets at 900°C as a function of the exposure time. The corresponding values for the Ni(40 vol%)/8YSZ, 8YSZ5T and 8YSZ10T [7] are also illustrated here.

The scatter in electrical conductivity values appearing at the beginning of the experiments among the samples is attributed to the difference in the porosity, reflecting the final stage of cermets preparation as well as to the structure configuration of the metal network depending on the oxide's proportions in the ceramic phase. A significant factor for the evaluation of the cermet stability after long term annealing is the difference between the initial (0 h) and the final (1000 h) electrical conductivity values. Ni/8YSZ cermets show the highest decrease in conductivity reaching the lowest values after 1000 h of exposure. Cermets with increasing TiO₂ content reach a steady state value at higher level within the first 500 h of exposure, while increased Y₂O₃ percentage influences negatively the electrical conductivity in general, reducing the final values.

Microstructure examination of 40 vol% Ni cermet samples after the exposure experiment, on which the electrical properties are determined, is performed by digital image analysis. Table III lists the results concerning the mean diameter, $\bar{d}$ of the Ni particles before ($t = 0$ h) and after ($t = 1000$ h) exposure at 1000°C in Ar/4%H₂ atmosphere. From the results it is evident that there is a significant difference in the increase of the mean Ni particle mean diameter, $\bar{d}$, between the

TABLE III Mean Ni particles diameter, $\bar{d}$, before and after annealing at 1000°C for 1000 h in Ar/4%H$_2$ atmosphere of the Ni(40 vol%)/mixed oxide cermets

Systems	$\bar{d}_{Ni,0h}$ (μ m)	$\bar{d}_{Ni,1000h}$ (μ m)	$\bar{d}_{Ni,1000h}/\bar{d}_{Ni,0h}$
Ni/8YSZ	1.56	3.11	1.99
Ni/8YSZ5T	1.65	1.98	1.20
Ni/8YSZ10T	1.62	1.83	1.13
Ni/12.5YZ15T	1.17	1.36	1.16

Ni/8YSZ (factor 2) and Ni/YZT cermets (factor 1.1–1.2).

According to the wetting results, the addition of lower surface energy TiO$_2$ in the ceramic matrix reduces the interfacial energy resulting in lower agglomeration tendency of Ni particles. The increased bond strength at the metal/ceramic interface influences positively the establishment of an improved continuous metallic network through the cermet. The sustained electrical conductivity values, attributed to the increased structure stability of the cermets, improve the long term stability of the SOFC anode.

4. Conclusions

Combined literature and experimentally measured contact angle data are used to evaluate the influence of TiO$_2$ and Y$_2$O$_3$ content on the surface properties of YZT oxides as well as on their interfacial behavior in contact with liquid Ni at 1500°C in Ar/4%H$_2$ atmosphere. The increased presence of TiO$_2$ in the mixed oxides improves wetting and reduces the surface and interfacial energy in the Ni/mixed oxide systems. On the contrary, the increase of Y$_2$O$_3$ content in the mixed oxides influences negatively the wetting behavior. The surface γ_{SV}, and interfacial γ_{SL}, energy values of the systems examined are calculated from the measured contact angles. The improvement of the bond strength at the metal/ceramic interface, caused by the presence of TiO$_2$, reduces the coarsening tendency of the Ni particles thus enhancing the structure stability of the SOFC anode cermets. Electrical conductivity measurements on Ni(40 vol%)/mixed oxides cermets shows that the values remain constant after annealing at 1000°C in Ar/4%H$_2$ atmosphere for 1000 h in contrast to the "state of the art" anode Ni(40 vol%)/8YSZ where a significant decrease is observed. Furthermore the increased TiO$_2$ presence in the ceramic phase is accompanied by a decrease of the TEC values of the Ni/YZT cermets adjusting to the TEC values of the 8YSZ electrolyte of the SOFC.

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