INFLUENCE OF ADDITIVES ON INTERFACIAL PROPERTIES BETWEEN Ni AND YSZ

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ABSTRACT

The properties of the interface between Ni and YSZ can be influenced by the addition of reactive elements (Ti, Cr, Mn and Pd) to the Ni or the use of an interlayer consisting of the oxides of the reactive elements. Wettability experiments (1500°C) showed the lowest contact angle (θ=103°) for the system YSZ/TiO₂/Ni. The carbon activity in metallic melt causes reduction of the oxide at the interface, leading to improved wetting conditions. This interaction is enhanced with increasing time and carbon activity. The reaction products were identified by EPMA and interpreted by thermodynamic considerations.

INTRODUCTION

The material most commonly used for the anode of the Solid Fuel Oxide Cell (SOFC) is a nickel/yttria stabilized zirconia (YSZ) cermet[1]. For long-term cell operation the main problem observed is the agglomeration of Ni, resulting in a decrease of the three-phase boundary areas of the electrode and electronic conductivity and consequently in a deterioration of cell performance. The rate of agglomeration increases with increasing nickel content in the anode. In general, the rate of sintering can be influenced through the particle-size distribution of both components of the cermet. Since nickel particles are high-surface-area solids, there is always a thermodynamic driving force to decrease free energy, i.e., to minimize surface area. In comparison to the reference Ni/YSZ anode several modifications or alternatives have been studied. The most promising modification seems to be the doping of YSZ with TiO₂ [2-4].

Reactive elements such as Ti, Cr, Mn and Pd were used as alloying elements for Ni or in the form of oxide interlayers between Ni and YSZ for the modification of the interface of the system. Wettability experiments were carried out at 1500°C in order to examine the wetting properties and the interfacial reactions of the systems.
EXPERIMENTS

Discs ($\Omega = 20 \text{ mm}$, $d = 130 \mu\text{m}$) of high-purity $\text{ZrO}_2$ stabilized with $\text{Y}_2\text{O}_3$ (8 mol%) (YSZ) ceramic were fabricated by foil casting and subsequent dense sintering at $1600^\circ\text{C}$.

High-purity metals were used, containing about 100 ppm carbon, employed in the form of targets for the sputtering of thin films ($\approx 2\mu\text{m}$) and cylindrical ingots for the wetting experiments. The reactive elements (Ti, Cr, Mn) and Pd were alloyed with Ni for 2 wt.% with the exception of Cr which was alloyed for 5 wt.%. The films of the alloyed Ni with the additives were oxidized at $1250^\circ\text{C}$ in air for 2h and in this way modified the surface of YSZ.

Wetting experiments were performed in an inductive furnace coupled alternatively with a molybdenum or a graphite susceptor in flowing Ar+4% vol. H$_2$ and purified Ar atmosphere respectively, at $1500^\circ\text{C}$.

RESULTS

Wetting experiments performed in an inductive furnace coupled alternatively with a molybdenum, in flowing Ar+4vol%H$_2$ atmosphere, or a graphite susceptor, in flowing Ar atmosphere for 45 min.

In first case no reaction observed at the interface for all examined systems. Table I summarizes the contact angles measured for each system indicating non-wetting conditions ($\Theta>90^\circ$). The lowest contact angle ($103^\circ$) was found for the system YSZ/TiO$_2$/Ni.

When a graphite susceptor was used as secondary coil in the inductive furnace, an interfacial reaction was observed for all examined systems, Fig. 1, concerning the carbothermal reduction of the ceramic substrate (see Discussion), [5]. The metallic elements Zr and Y, dissolved in the Ni melt according this reaction, were reoxidized into the metallic drop during the cooling process forming oxide precipitations, Fig 1, with a Zr/Y ratio different from that of YSZ materials. Table II illustrates the Zr/Y ratios of the oxide phases present in each system and measured by EPMA. The contact angles were found in this case to be lower than under non-reactive conditions, Table I.

DISCUSSION

a) Interfacial reaction and interpretation of EPMA measurements

When a graphite susceptor was used for the experiments this material can partly react with the residual moisture of the protective atmosphere (flowing Ar) creating in this way a carbon potential in the furnace atmosphere. At the temperature of $1500^\circ\text{C}$, it is known that Ni dissolved about 11wt.% carbon, [6]. According to
thermochemical calculations for the used experimental conditions the carbon activity into the metallic phase is of a magnitude of $10^{-5}$ and acts as reducing agent for the reduction of the ceramic substrate (Fig 2) according to the reaction schemes proceeding at the metal-ceramic interface:

$$\begin{align*}
\text{ZrO}_2 + 2[\text{C}]_{\text{Ni}} &= [\text{Zr}]_{\text{Ni}} + 2[\text{CO}]_{\text{Ni}} \\
\text{Y}_2\text{O}_3 + 3[\text{C}]_{\text{Ni}} &= 2[\text{Y}]_{\text{Ni}} + 3[\text{CO}]_{\text{Ni}}
\end{align*}$$

(1)  
(2)

The above described reaction mechanism is confirmed by the fact that no interfacial reaction takes place when no carbon was present in the furnace atmosphere (use of Mo susceptor). Further wetting experiments carried out in a high-frequency furnace with a graphite susceptor under flowing Ar+4vol%H$_2$ confirmed also the above consideration. Under these experimental conditions the reaction of the graphite with the hydrogen of the protective atmosphere according to the scheme:

$$\text{C} + 2\text{H}_2 = \text{CH}_4$$

(3)

results to the development of a much higher carbon activity in the furnace atmosphere and consequently into the metallic melt. Thermodynamic calculations estimated this value to be $a_c=0.407$. This value is significantly higher than the value for the case of flowing Ar resulting in a more extensive interaction at the metal-ceramic interface, appeared to be progressed with the time, leading an extensive attack of the ceramic. The extend of the interfacial reaction influences the wetting properties of the system. Thus for the system YSZ/Ni(Ti) the value of the contact angle measured during the wetting experiment decreased with the time and reached after 45 min a value of 30°. Fig 3 illustrates the time dependence of the this value measured in this case.

According to the reaction scheme described above and the thermochemical calculations, all oxides of the solid solution including those of the reactive additives, can be reduced under the experimental conditions. The metals and the oxygen remain dissolved in the metallic melt. At the beginning of the cooling process according to thermochemical data Y$_2$O$_3$ dissolution limits are reached firstly resulting in the coprecipitation of oxides of Y$_2$O$_3$ and ZrO$_2$ presenting a Y/Zr ratio significantly higher than that of the reference YSZ material (see Table II). Under these conditions the non-reacted ceramic residues in the interaction zone form crystallization nuclei for the oxides ZrO$_2$ and Y$_2$O$_3$. This explains the variation of Zr/Y atomic ratios found by the EPMA point measurements at different positions in the erosion zone, as can be seen from the experiments with Ni-Mn and Ni-Pd alloys (Table II).

Oxide phases strongly enriched in Y$_2$O$_3$, compared to the reference YSZ material, can also be formed inside the metal drop. This results in a decrease of Y concentration in metallic melt and therefore a further decrease of the temperature leads to the formation of oxide phases consisting mainly of ZrO$_2$ and explaining some of the higher Zr/Y values of the precipitations inside the metal drop. At the surface of the drop even nearly pure ZrO$_2$ was found (Zr/Y>100). This is possibly due to the rapid cooling
process on the skin of the liquid metal where the oxidation of Y is much faster so that an increase of dissolved Zr metal can be produced.

b) Influence of additives on interfacial reaction and wetting properties

According to the contact angle values shown in the first column (Mo) of Table I the addition of the selected active elements makes a positive contribution to the wetting properties of the YSZ/Ni system, disregarding the following exceptions. When Ti and Mn were used as alloying elements for Ni, high contact angles were measured. These two elements are most reactive in comparison to Cr and Pd. Under the experimental conditions the oxygen potential in the environmental atmosphere is high enough for these elements to result in the formation of an oxide layer on the drop surface, as could be observed, which prevents the spreading of the drop. Cr and Pd were not oxidized under the same conditions.

When the additives were used in the form of an oxide on the YSZ surface in general a smaller contact angle was observed in comparison to the pure YSZ surface. The oxides of the active elements Ti, Mn, and Cr show a trend to diffuse into YSZ. An analysis of the cross sections of the samples by EDAX revealed that Ti could be detected up to a distance of 8 μm from the free surface of the YSZ substrate. Detectable quantities of Mn and Cr were even also found at a depth of 30 and 20 μm respectively. From this point of view the contact angles determined by the wetting experiments can be interpreted in such a way that the higher the concentration of the active elements on the surface of the YSZ ceramic the higher the potential to improve the wettability of this system.

The extent of the interfacial reaction, which took place when a graphite susceptor was used, did not seem to be influenced by the presence of additives except in the case of Mn. The extent of the reaction was about 9 μm for all other systems including YSZ/Ni while using Mn as an oxide interlayer or as alloying element for Ni and the extent of the interaction zone was measured as 18 and 27 μm respectively. It can therefore be concluded that Mn in the immediate vicinity of the interface enhanced the reduction of the substrate.

According to Laurent [7] the lowest contact angle which could be observed in a reactive system is given by:

$$\cos \Theta_{\text{min}} = \cos \Theta_0 - (\Delta \gamma_f/\gamma_v) - (\Delta G_r/\gamma_v)$$

(4)

where $\Theta_0$ is the contact angle under non-reactive conditions, $\Delta \gamma_f$ is the changed interfacial energy due to the interfacial reaction, $\Delta G_r$ is the change of free energy per unit area released by the interfacial reaction and $\gamma_v$ is the surface energy of the molten metallic phase.

Since for all examined systems the reaction at the interface is the same, the reduction of YSZ, it is concluded that the change in interfacial energy is the
predominant contribution to reactive wetting. According to the results of the second column (graphite) of Table I it is concluded that the dissolution of Mn₃O₄ into the YSZ crystal has the most positive influence on the change of the interfacial energies under reactive conditions, thus also giving the lowest contact angle of 89°. The wetting experiments between the YSZ ceramic and the Ni-based melts differ from the operating conditions in the anode of a SOFC. Nevertheless the observed influence of active elements as additives in the YSZ system leads to the assumption that also the solid-solid interface of the anode cermet can be positively influenced. Long-term experiments under real conditions have been planned to investigate this phenomenon.

CONCLUSIONS

Wetting experiments between Ni-based melts and YSZ substrates at 1500°C have shown that active elements, such as Ti, Cr, Mn and Pd alloyed to Ni or used as oxides modifying the YSZ surface, positively influence the interfacial energy of this system. This effect seems to be small under these conditions.

Much higher is the influence of dissolved carbon in the melt, which can react and reduce the YSZ ceramic. High carbon concentration revealed large interaction effects and consequently results in good wettability of the system.

It is necessary to examine the influence of those effects under real anode temperature conditions where the possibility of interaction is negligible.

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Table I: The contact angle of various metallic melt / ceramic systems measured at 1500°C using different susceptor materials resulting in different reducing potentials

| System                | Molybdenum susceptor | Graphite susceptor |
|-----------------------|----------------------|--------------------|
|                       | non-reactive         | reactive           |
| YSZ/Ni                | 117                  | 105                |
| YSZ/TiO₂/Ni           | 103                  | 98                 |
| YSZ/Ni,Ti             | 129                  | 107                |
| YSZ/CoO₃/Ni           | -                    | 117                |
| YSZ/Ni,Co             | 108                  | 100                |
| YSZ/Mn₃O₄/Ni          | 111                  | 89                 |
| YSZ/Ni,Mn             | 123                  | 103                |
| YSZ/Pd-PdO/Ni         | 113                  | 108                |
| YSZ/Ni,Pd             | 113                  | 101                |

Table II: Zr/Y atomic ratio measured by EPMA on cross-sections of the specimens of the wetting experiments with a graphite susceptor in an Ar atmosphere at 1500°C.

| System               | Precipitation on the drop surface | Precipitation inside the drop | Erosion zone of YSZ ceramic | Ceramic substrate |
|----------------------|----------------------------------|-------------------------------|-----------------------------|-------------------|
| YSZ/Ni               | 30 ... >100                      | 2.3...2.9                     | 1.8...2.6                   | 5.4               |
| YSZ/TiO₂/Ni          | -                                | 1.9...2.7                     | 1.6...3.1                   | 6.1               |
| YSZ/Ni,Ti            | 5.2 ... >100                     | 1.1...2.2                     | 5.3...6.0                   | 5.6               |
| YSZ/CoO₃/Ni          | 6.8...>100                       | without                      | 5.3...5.7                   | 5.6               |
| YSZ/Ni,Co            | 1.7...22                         | 1.7...6.8                     | 4.5...5.3                   | 5.3               |
| YSZ/Mn₃O₄/Ni         | -                                | 3.1...4.6                     | 1.7...5.8                   | 5.8               |
| YSZ/Ni,Mn            | 2.6 ... >100                     | 2.0 ... 4.3                   | 1.1 ... 5.6                 | 5.5               |
| YSZ/Pd-PdO/Ni        | 9.6...47                         | without                      | 5.6...5.9                   | 5.9               |
| YSZ/Ni,Pd            | 5.6 ...>100                      | 1.8 ... 5.5                   | 1.1 ... 5.7                 | 5.7               |

Zr/Y>100 is nearly pure ZrO₂ (Y<0.3 at.%)
\[ W_a = \gamma_{LV} \times (1 + \cos \Theta) \]

Fig. 1 Scheme of a sessile drop and micrographs of cross-sections from
(a) the surface-near region and
(b) the interface between molten metal and YSZ
Fig. 3  Time dependance of the contact angle measured for the system YSZ/Ni,Ti at 1500°C in a HF furnace coupled with a graphite susceptor in a flowing Ar+4vol%H₂ atmosphere.
Fig. 2. Thermochemically calculated CO partial pressure at various temperatures for the carbothermal reduction of different metal oxides to pure metal.