CONSIDERATIONS ON THERMAL EXPANSION OF NICKEL-ZIRCONIA ANODE IN SOFC DURING FABRICATION AND OPERATION

Masashi Mori, Tohru Yamamoto, Hibiki Itoh,
Central Research Institute of Electric Power Industry
2-6-1 Nagasaka, Yokosuka Kanagawa 240-01 Japan
Hideaki Inaba and Hiroaki Tagawa
Institute of Environmental Science and Technology, Yokohama National University,
156 Tokiwadai, Hodogaya-ku, Yokohama Kanagawa 240 Japan

ABSTRACT

The expansion characteristics of NiO-8 mol% yttria stabilized zirconia (8YSZ) composites and Ni-8YSZ cermet in air and a hydrogen atmosphere have been investigated in the temperature range 50-1000 °C. The thermal expansion coefficients (TECs) of NiO-8YSZ composites in air increased monotonously with increased NiO content over the whole composition in the NiO-8YSZ system. Under the H2 atmosphere, NiO in the composites was changed into Ni, and their expansions were affected by the reduction of NiO. The TECs of Ni-8YSZ cermet in the H2 atmosphere were governed strongly by that of each matrix. For the cermet used for measurement in air, the nickel particles were drastically oxidized into NiO over 900 °C, and as a result, many cracks occurred in the samples.

INTRODUCTION

The SOFC configuration can be classified into two types, planar and tubular. Of all the configurations, the development of planar type SOFC is being given new attention due to its high power density and ease of application of cheap fabrication methods. In the case of planar type SOFC, the stacks are fabricated using three separator cell-components: single cells consisting of anode, electrolyte and cathode, separator plates, and sealing materials. The anode material, at first, is a composite of nickel oxide and yttria stabilized zirconia (YSZ) during the fabrication process. The components, in general, are fabricated into the stack during heat treatment at a rather high temperature (≥1100 °C) under an oxidizing atmosphere, namely, air. When fuel gas is supplied into the stack, the anodes are exposed to reducing atmosphere and the composite is changed into a cermet of nickel metal and YSZ.

Since reduction from NiO to Ni means a decrease of volume, an understanding of the expansion behavior is quite important to prevent an occurrence of thermal stress in
the stack. In addition, the thermal expansion of Ni-YSZ cermet must be close to those of the other cell components. Even though the Ni-YSZ cermet anodes have been used by SOFC researchers, only little work has been published about the fundamental expansion properties [1,2]. The aim of this paper is to study the influence of composition of NiO-YSZ composites and Ni-YSZ cermets on thermal expansion behaviors with a view point of the fabrication and operation in the SOFC.

EXPERIMENTAL

The NiO-YSZ composite powders were prepared by using ordinary ceramic powder preparation method. Starting material powders, NiO powder (>99 %, Nakalai Chem., Japan) and 8 mol% yttria stabilized zirconia powder (8YSZ)(>99.9 %, Toso, Japan) were used without further purification. The powders in the desired proportions were thoroughly mixed with ethanol in a rotary-type yttria partially stabilized zirconia ball mill for 48 h. After being dried, the mixtures were pressed into a tablet under 40 MPa. To obtain the dense tablets with relative densities ≥95 %, they were finally fired at 1500 °C for 5 h in air.

The average linear TEC was measured by using two Mac Science TD-5000S equipment in the temperature range from 50 to 1000 °C. The samples were cut into a columnar shape (5 mm φ X 20 mm length). References used in these measurements were a fused-silica for the measurements in air and sapphire for the measurement in hydrogen. A heating rate of 2 °C/min and a flow rate of 100 ml/min of hydrogen gas were used in these measurements after being bubbled in pure water at 10 °C. Measurements were performed stepwise and sweepingly. For the stepwise method, there was a holding time of 30 minutes at each 100 °C.

After the NiO-YSZ composites are measured in the H₂ atmosphere, the Ni metal vol% in the samples shows different values from those of the composites because of a change of density between Ni and NiO and the formation of pores. The compositions and relative densities of the samples in this study are summarized in Table 1. The compositions (vol%) of 8YSZ and NiO in Table 1 were calculated as samples without pores.

RESULTS AND DISCUSSION

The microstructure in the composites consists of small NiO particle sizes of 2-8 μm. There is no doubt that NiO acts as a matrix for the composite in place of 8YSZ at the composition of about 50 vol%NiO. A formation of connection of NiO particles in the grain-boundary in the 8YSZ matrix started at around 30 vol% NiO according to the theory of percolation [3]. It was confirmed by SEM photographs that the NiO and 8YSZ particles were distributed homogeneously in each matrix.
After the cell components of the SOFC are bonded at high temperature, the anodes of the single cells are a composite of NiO and 8YSZ and are cooled down in air. Therefore, the TEC of NiO-8YSZ composite in air is one of the very important factors. Fig. 1(a) shows the TECs of 8YSZ, 52 vol%NiO-8YSZ composite and NiO in air as a function of temperature. The TECs were derived from data of thermal expansions at each 5 °C. For the 8YSZ, an increase of TECs with temperature was observed because of the formation of point defects in the structure. On the other hand, there is a peak in the TEC curves of the NiO and the composite. Thermal expansion of NiO has been measured by many researchers [4]. NiO is well known to become paramagnetic from antiferromagnetic above 257 °C [5]. Recently, Inaba [6] also reported that since a magnetic property and a change of ionic valence in materials affect the thermal expansion strongly, the peak in the TEC curve corresponds to the Neel temperature of NiO. However, the crystal structure of NiO is based on the NaCl type and the phase transformation from rhombohedral to cubic is observed at 250 °C [7]. Taking into account these factors, it is most likely that the peak at approximately 250 °C contains the effect of both the magnetic transition and the phase transformation.

Fig. 1(b) shows the thermal expansions of the 8YSZ, NiO-8YSZ composites and NiO in air by using the sweeping method. The curve of the composites with ≥30 vol%NiO exhibited a slight change in the vicinity of 200-250 °C, and the tendency increased with increased NiO content. As mentioned above, the change in the expansion curve can be explained by the magnetic transition and the phase transformation. Fig. 1(c) shows the average linear TECs of the NiO-8YSZ composites from 50 to 1000 °C in air in comparison with the simplest model of rule of mixtures (1):

\[ \ln P_e = V_i \ln P_i + (1-V_i) \ln P_m \]  

where P is the TEC and V is the volume fraction [8]. The suffixes c, i and m stand for the composite, inducing material and matrix, respectively. The solid line represents the calculated results for the simplest model. The TECs were 10.3X10⁻⁶/°C for 8YSZ and 14.2X10⁻⁶/°C for NiO. The TECs of the composites increased monotonously with increased NiO content and were close to that of NiO. These results agree with the calculation of the rule of mixtures for the composites.

Fig. 2(a) shows the expansions of the NiO-8YSZ composites in the H₂ atmosphere by using the sweeping method. When the SOFC generator generates electricity using the fuel gas for the first time, NiO in the composite anode is reduced into Ni. The experimental condition is similar to the actual one in the SOFC operation. In the measurement, NiO in the composites was changed into Ni metal at above 500 °C. The NiO reduction effect on the expansion behavior was remarkable for heavy NiO-content (NiO > 30 vol%). On the other hand, no anomalies in the expansion behaviors were observed in the region of NiO ≤ 20 vol%. This is due to no formation of connection of NiO particles in the sample. These expansions in the temperature range 50-1000 °C were expressed as average linear TECs, and the values are shown in Fig. 2(b). Since the TEC of 8YSZ is constant regardless of oxygen partial pressure, the TECs of 8YSZ in air and the H₂ atmosphere showed the same values. In the region of
0 vol% < NiO < 60 vol%, the TEC of the cermets increased drastically with increased NiO content. The TECs of the composites with 60 vol% ≤ NiO ≤ 80 vol% showed an independence on the NiO reduction because of the shrinkage of Ni particles in the samples. It can be seen in Fig. 2(c) that the addition of 8YSZ into NiO matrix prevents the shrinkage of the sample by the NiO reduction.

Fig. 3 shows the expansion of the 50 vol% NiO-8YSZ composite in the H2 atmosphere by using the stepwise (—) and sweeping (○) methods. It should be noted that in the measurement by the stepwise method, a remarkable increase in thermal expansion was observed at around 500 °C. The volume change was observed for the composites with the content of NiO ≥ 30 vol% and increased with increased NiO content. In the temperature range from 50 to 400 °C, the TECs of NiO-8YSZ in air and the H2 atmosphere were equal, and the TECs of the samples in the temperature range ≥ 600 °C also corresponded to those of the cermets in the H2 atmosphere. Although the composites with NiO ≥ 90 vol% shrank greatly, the others showed noticeable expansion in the reducing atmosphere.

In order to make clear the volume change, microstructures of the samples after the H2 measurements were observed. After the 52 vol%NiO-8YSZ composite, that is, the 40 vol%Ni-8YSZ cermet was reduced in the H2 atmosphere at 1000 °C for 30 minutes, its SEM photograph is shown in Fig. 4. The nearly white part in the figure shows a matrix of 8YSZ, and the black part shows pores formed by reducing NiO particles. The intermediate color between white and black shows Ni metal particles. Ni particles are smaller in comparison with those of NiO before reduction. However, the TEC of Ni in the H2 atmosphere is much larger than those of 8YSZ and NiO in air. Therefore, we conclude as follows. NiO particles are reduced into Ni particles above 500 °C under reducing atmosphere. Although once shrinking, the Ni particles expand their original lengths at the high temperatures immediately. Then, the connection of Ni particles which have a plastic deformation should protrude from a framework of 8YSZ, and the expansion should affect the volume change.

During operation, the SOFC generator is cycled many times to approximately room temperature and back to operating temperature. Then, the nickel keeps a metal state and the Ni-8YSZ cermet anode sustains the thermal cycle. Fig. 5(a) shows the TECs of 8YSZ, 40 vol%Ni-8YSZ cermet and Ni in the H2 atmosphere as a function of temperature. A peak in the TEC curve of Ni was observed at about 360 °C. Since it is well known that Ni is ferromagnetic and its Curie temperature is 358 °C, the peak is related with it. Fig. 5(b) shows the thermal expansion of the Ni-8YSZ cermets in the H2 atmosphere, and the TECs of the cermets from 50 to 1000 °C are also shown in Fig. 5(c). The TEC of Ni metal was 16.9X10^-6/°C and this value is in good agreements [9]. Observed increase of TECs with increased Ni content in the region of 0 vol% ≤ Ni ≤ 60 vol% was, however, not drastic, whereas the TECs in the composition range > 60 vol%Ni increased drastically with increased NiO content. The reason for this is as follows. Because of a large difference of the TECs between Ni and 8YSZ in the H2 atmosphere, a shear strain occurs at the interface between 8YSZ and Ni particles. However, the Young’s modules of Ni is quite larger than that of 8YSZ so that the deformation of Ni metal could relax the strain [10,11]. The TECs of the cermets were
subjected to those of stiff matrix of 8YSZ, not ductile Ni connection in the matrix. In this case, the TECs of the cermets can be expressed by the Kerner's equation (2):

$$\alpha_c = \sum \alpha_i V_i + 4 \frac{G_m}{K_c} \sum \frac{K_c - K_i}{4G_m + 3K_i} (\alpha_m - \alpha_i) V_i$$

(2)

where K is the bulk modulus, G is the shear modulus, and V is the volume fraction [11]. The suffixes are the same as in equation (1). A fitting between the results in this study and the Kerner's equation for TECs is in progress.

It is expected that an SOFC generator will operate at high fuel utilizations and will experience emergency shutdown. Then, the anode will be exposed to high oxygen partial pressures which will enable Ni metal in the cermet to oxidize. Fig. 6(a) shows the expansion of the 35 vol%Ni-8YSZ cermets in air by using the sweeping (—) and stepwise (O) method, and their expansions from 50 to 1000 °C are plotted as average linear TECs in Fig. 6(b). The expansion started gradually at approximately 600 °C, and a drastic increase of expansion was observed at approximately 900 °C. This behavior obviously relates with the Ni oxidation in the cermets: A weight increase of the Ni-8YSZ cermets by the Ni oxidation metal was observed in the thermogravimetry (TG) analysis. Figs. 6(c) and (d) show the SEM photographs of the 40 vol% Ni-8YSZ cermet after oxidizing at 1000 °C for 30 minutes. A self-destruction of some samples was also observed in the thermal expansion measurement (Fig. 6(c)) and many cracks along the grain-boundary of 8YSZ matrix were observed (Fig. 6(d)). These results suggest that the Ni-8YSZ cermet in the SOFC stack should never be exposed to the oxidizing environment in the temperature range ≥600 °C after reducing NiO in the anode assuming no TEC dependence on the porosity in the Ni-8YSZ cermets is observed.

CONCLUSION

The TECs of the dense NiO-8YSZ composites have been investigated in air and the hydrogen atmosphere in the temperature range from 50 to 1000 °C. A high concentration of NiO in the composites causes a different TEC from 8YSZ electrolyte in air, and it gives larger volume change because of a large TEC of Ni metal in the reducing atmosphere. When the Ni-8YSZ cermets are oxidized, a large expansion caused by Ni oxidation makes a lot of cracks in the sample. In the case of the anode without pores, the best composition of NiO content in the composites is thought to be in the vicinity of 40-50 vol%NiO to prevent the occurrence of thermal stresses in the SOFC stack.

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Table 1 Compositions (vol%) and relative density of NiO-8YSZ composites and Ni-8YSZ cermets.

| Sample  | NiO (vol%) | 8YSZ (vol%) | Ni (vol%) | 8YSZ (vol%) | relative density(1) | relative density(2) |
|---------|------------|-------------|-----------|-------------|--------------------|--------------------|
| 8YSZ    | 0          | 100         | 0         | 100         | ≥98 %              | 98 %               |
| 10NiO-8Y| 10         | 90          | 6         | 94          | ≥98 %              | 98 %               |
| 20NiO-8Y| 20         | 80          | 13        | 87          | ≥98 %              | 95 %               |
| 30NiO-8Y| 30         | 70          | 25        | 75          | ≥98 %              | 86 %               |
| 41NiO-8Y| 41         | 51          | 30        | 70          | ≥98 %              | 83 %               |
| 47NiO-8Y| 47         | 53          | 35        | 65          | ≥98 %              | 81 %               |
| 52NiO-8Y| 52         | 48          | 40        | 60          | ≥98 %              | 79 %               |
| 57NiO-8Y| 57         | 43          | 45        | 55          | ≥97 %              | 77 %               |
| 62NiO-8Y| 62         | 38          | 50        | 50          | ≥97 %              | 75 %               |
| 70NiO-8Y| 70         | 30          | 59        | 41          | ≥97 %              | 71 %               |
| 80NiO-8Y| 80         | 20          | 71        | 29          | ≥97 %              | 67 %               |
| 90NiO-8Y| 90         | 10          | 85        | 15          | ≥97 %              | 63 %               |
| NiO     | 100        | 10          | 100       | 0           | ≥88 %              | 58 %               |

Relative densities in the table mean the values of samples in air for (1) and in the H₂ atmosphere for (2).
Fig. 1(a) TECs of 8YSZ, the composite and NiO in air as a function of temperature.

Fig. 1(b) Thermal expansions of the 8YSZ, NiO-8YSZ composites and NiO in air.

Fig. 1(c) Average linear TECs of the NiO-8YSZ composites from 50 to 1000 °C in air in comparison with the simplest model of rule of mixture.

Fig. 2(a) Expansions of the NiO-8YSZ composites in the H₂ atmosphere by using the sweeping method.
Fig. 2(b) Average linear TECs of the NiO-8YSZ composites from 50 to 1000 °C in the H₂ atmosphere.

Fig. 2(c) Expansions of 90 vol%NiO-8YSZ composite and NiO in the H₂ atmosphere.

Fig. 3 Expansion of the 50 vol%NiO-8YSZ composite in the H₂ atmosphere.

Fig. 4 SEM photographs of the 40 vol%Ni-8YSZ cermet after reducing in the H₂ atmosphere at 1000°C for 30 minutes.
Fig. 5(a) TECs of 8YSZ, the cermet and Ni in the H₂ atmosphere as a function of temperature.

Fig. 5(b) Thermal expansion of the 8YSZ, composites and Ni in the H₂ atmosphere.

Fig. 5(c) Average linear TECs of the Ni-8YSZ cermets from 50 to 1000 °C in the H₂ atmosphere.

Fig. 6(a) Thermal expansion of the 35 vol%Ni-8YSZ cermet in air by using the sweeping and stepwise method.
Fig. 6(b) Average linear TECs of the Ni-8YSZ cermets in air by the sweeping method.

Fig. 6(c) SEM photographs of the 40 vol%Ni-8YSZ cermet after the measurement in air.

Fig. 6(d) SEM photographs of the 40 vol%Ni-8YSZ cermet after the measurement in air.