PREPARATION OF POROUS NICKEL-TITANIA CERMETS AND THEIR APPLICATION TO ANODE MATERIALS

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ABSTRACT

Porous nickel-titania cermets have been prepared as new-type anode materials for solid oxide fuel cells using the solid-state displacement reaction method. The microstructures of the cermets were interwoven aggregate-type, differently from those of conventional nickel-YSZ cermets: nickel and titania phases three-dimensionally entangled each other. These cermets revealed good properties in compatibility of thermal expansion with YSZ, strength, gas permeation and electrical conduction.

INTRODUCTION

Planar solid oxide fuel cells (SOFC) have intensively been investigated because of their high power density in comparison with tubular ones, and two types of cell construction are being developed: one is self-supported type in which a cathode/electrolyte/anode tri-layer is supported by two separators and the other is substrate type in which a thick anode substrate with thin cathode and electrolyte layers on its surface was put between two separators. Since the substrate type planar SOFC is stronger than self-supported type one, the former is superior in constructing large capacity cells (1). In the substrate type SOFC, however, good compatibility of thermal expansion with zirconia electrolyte and high strength is required for anode materials. Though nickel-zirconia cermets are recommended as anode materials, the thermal expansion coefficient is higher than that of zirconia electrolyte due to nickel phases with a high thermal expansion coefficient. Recently, we found that this problem could be solved by replacement of zirconia with titania (TiO$_2$) with a lower thermal expansion coefficient than zirconia and that, in Ni-TiO$_2$ cermets, microstructures with
high strength and high electrical conductivity could be obtained. In addition, this material showed high catalytic activity as the anode: the electrode resistivity in a Ni-TiO$_2$ cermet/plasma-sprayed zirconia film system was less than 0.1 $\Omega \cdot$cm$^2$ in a H$_2$/H$_2$O stream even at 800 °C.

When metallic phases of the cermet have a three-dimensional network arrangement, the strength and electrical conductivity become higher than those of cermets with island-like arrangements like conventional nickel-zirconia cermets. Nickel-titania cermets with such microstructures can be prepared by the solid-state displacement reaction method (2) which is a new technique developed for making metal-oxide composites. A composite consisting of the metal Me and the oxide M$_x$O is conventionally made by mixing metal Me and oxide M$_x$O powders and sintering their compact at a high temperature. In the solid-state displacement reaction method, on the contrary, the compact of mixed metal M and oxide Me$_y$O powders is annealed at a high temperature to cause the reaction $x$M + Me$_y$O = M$_x$O + yMe and the Me-M$_x$O composite is obtained. This composite has a unique microstructure with an interwoven-aggregate or island-like arrangement of metallic and oxide phases according to a combination of metals and oxides to be allowed to react; conclusively, the microstructure depends on the diffusion rate of reaction species. In the reaction of NiO and Ti, the microstructure of the product is interwoven-aggregate type and will answer for our purpose. In this study, therefore, conditions for preparing Ni-TiO$_2$ cermets and their properties have been investigated in order to apply them to anode materials for the substrate-type planar SOFC.

EXPERIMENTAL

The powders of NiO (99.9 %, 2 $\mu$m) and Ti (99.5 %, -350 and -100 mesh) were mixed with the molar ratio 2:1, assuming the displacement reaction 2NiO + Ti = 2Ni + TiO$_2$, and pressed under 50 to 200 MPa. The compacts were annealed in argon at 1000 to 1400 °C for 2 to 25 h. The annealed specimens were analyzed with a powder X-ray diffractometer to identify the reaction products and with an electron probe microanalyzer to observe and analyze the products. The properties of the specimens were examined for thermal expansion coefficient, four-point bending strength at room temperature, N$_2$ gas permeability at room temperature and electrical conductivity.

RESULTS AND DISCUSSION

Microstructure

The microstructure of a specimen (Ti -350 mesh) after annealing at 1000 °C for 25 h is shown in Figure 1. The gray phases in the figure is rutile-type titanium dioxide TiO$_2$ and the white phases is nickel containing titanium less than 1 at.%. No other product was detected. These facts show that the reaction 2NiO + Ti = 2Ni + TiO$_2$ perfectly proceeded during annealing. The nickel phases three-dimensionally entangles
each other to form a network structure. Many small pores were found in TiO₂ phases. The pores became fewer as the annealing temperature was raised. The porosity, as shown in Figure 2, decreased with increasing annealing temperature and applied pressure were raised.

**Thermal Expansion Coefficient**

Thermal expansion coefficient was measured in argon in the temperature range of room temperature to 1000 °C. The specimens expanded almost linearly; above 300°C, the coefficient was constant. The average thermal expansion coefficient from room temperature to 1000 °C was 11.3 × 10⁻⁶ K⁻¹ and is very close to that for yttria-stabilized zirconia (3).

**Bending Strength**

The strength of the cermets prepared under various conditions was measured by four-point bending. The relation between bending strength and porosity is shown in Figure 3. The measured values of the bending strength fall on a curve independently of the applied pressure, annealing temperature and particle size of titanium powder. The strength decreases with an increasing porosity. The anode is required to have high gas permeability. In the porosity range of 0.30 to 0.36, the N₂ permeability was 10⁻² to 10⁻³ cm³·g⁻¹·s⁻¹ at room temperature, being sufficiently high for gas permeation. The strength is about 100 MPa at a porosity of 0.30 and about 70 MPa at a porosity of 0.36 from the figure. The bending strength value 100 MPa at a porosity of 0.30 is considered to be sufficient to construct the substrate-type planar SOFC.

**Electrical Conductivity**

The electrical conductivity was measured by the dc four-probe method in hydrogen saturated with water vapor at 30 °C. The change in the electrical conductivity with temperature is shown in Figure 4 for the specimen with a porosity of 0.368. The electrical conductivity decreases sharply with increasing temperature to 300 °C; the slope changes at a temperature midway between 300 and 400 °C and becomes moderate above 400 °C. This transition is due to the magnetic transformation of nickel phases in the cermet (4).

Although the electrical conductivity of titania depends on both the temperature and oxygen pressure, it is negligibly low in comparison with that of nickel (5). Since the volume ratio of nickel and titania phases in the cermet, \( V_{\text{Ni}} / (V_{\text{Ni}} + V_{\text{TiO₂}}) \), is 0.41, nickel phases must conduct nearly all electricity. The electrical conductivity measured at every temperature was 0.044 times as high as that of pure nickel. In addition, the electrical conductivity hardly depended on the ratio of water vapor and hydrogen, i.e. on the oxygen pressure. These facts support that the electrical conduction occurs through nickel phases.

At 1000°C, the cermet has an electrical conductivity of about 1000 S·cm⁻¹, as already shown in Figure 4. This value is almost the same as the highest one reported
for nickel-yttria stabilized zirconia cermets (6, 7).

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Fig. 1  Microstructure of a specimen (Ti -350 mesh) after annealing at 1000 °C (a) and enlarged view (b).

Fig. 2  Relation between porosity and annealing temperature.
Fig. 3 Effect of porosity on bending strength.

Fig. 4 Change in electrical conductivity with temperature.