A STUDY ON STRUCTURE OF FUEL ELECTRODE FOR SOFC

Chikara IWASAWA, Masakatu NAGATA, Satoru YAMAOKA, Youko SEINO, Motoyuki ONO

Fujikura Ltd.
1-5-1, KIBA, KOTO-KU, TOKYO, 135, JAPAN

ABSTRACT

One of the major problems of SOFC is the sintering of Ni particles operation which causes the degradation of fuel electrode. To suppress the sintering of Ni particles, we have been trying to achieve homogeneous dispersion of Ni particles and fix them in the film. Ni/YSZ powder composed of Ni particles strongly combined with YSZ(Yttria Stabilized Zirconia) particles by mechanical milling techniques, etc., were studied, and some of powders proved to be effective for the suppression of the sintering of Ni particles.

INTRODUCTION

The solid oxide fuel cell (SOFC) is expected to be a next-generation power generating system which is clean and highly efficient. Fujikura has manufactured an electrode supporting member and investigated a film-producing method which uses a plasma-spray, etc (1,2,3,4). In this way it has become possible to promote the improvement of the cell output density. In order to prolong the life of the cell, ways to prevent the nickel used in the fuel electrode from sintering or coagulating have been investigated. This is thought to be one of the causes of deterioration during long-term power generation.

PROCESS SCHEMES

Features of various kinds of powder

The production method, feature and expected effects of the raw material now being investigated are as follows.

Mechanical milling method

In this method, nickel and YSZ (Yttria Stabilized Zirconia) are made into an

686
amorphous powder with the chemical composition kept constant. The composition can be controlled easily, and uniform structure can be obtained easily. Since nickel and YSZ are strongly bonded to each other, it is expected that the shape is not deformed even if it is passed through high-temperature gas in the plasma. Moreover, it is effective in preventing nickel from coagulating.

**YSZ coating method**

This method uses powder coated YSZ particles on nickel particles by physical coating (Hybridization). Hybridization disperses the powders in the gaseous phase and gives each powder mechanical/thermal energy effectively to embed or coat the fine powder onto the surface of core powder repeatedly by the function of a rotor which rotates with very high-speed in a circulation circuit for a very short time.

If you use the plasma spray method, you will find that nickel or nickel oxide whose melting point is lower than that of YSZ will melt and coagulate first. Because it has to pass through a high-temperature gas, it can be expected that uniform melting is obtained by coating YSZ on the surface of nickel.

**High-melting point material method**

Nickel is prevented from coagulating by coating nickel or YSZ on a high-melting point metal or ceramic which has high electric conductivity. Hybridization and the electroless point plating method were also investigated.

In this report, powder was actually produced by mechanical milling and the YSZ coating method and film production were investigated.

**EXPERIMENT**

**Raw-material production test**

**Mechanical milling method**

Two kinds of nickel particles approx. 1 to 2 μm in size and an average of approx. 9 μm in diameter, and YSZ particles 1 μm in size were prepared. They were mechanically milled with different times. The production conditions are shown in Table.1. The surface and cross-section of the finished raw material were observed for judgment. Thereafter, the oxidizing process (1,000 °C, 2 hours in air) was applied. If necessary, it is classified and is used as the raw material.

**YSZ coating method**

Several kinds of nickel particles in terms of particle size and shape (Table 2), and YSZ of approx. 1 μm in size were prepared. After these were mixed, coating was applied by the Hybridization method (Table.3) which is a physical method. After the
surface and cross section were observed, the oxidizing process was further applied. If necessary, it will be classified.

**Bulk and film-production method investigated**

For these raw materials, forming was executed with one-axis press and film production by the plasma spray method was investigated. The bulk and film were observed, and their electric conductivities were measured.

**RESULT**

1. Raw material production result

1.1 Mechanical milling method

A photomicrograph of the raw material produced is shown in Fig.1. As a result of the observations, it was found that nickel and YSZ were overlapped and laminated to each other. As nickel is smaller in particle size, nickel and YSZ tend to be dispersed earlier.

1.2 YSZ coating method

An SEM photo of the raw material produced is shown in Fig.2. From the results of observation, it was found that YSZ sticks well depending on the shape of nickel. Particularly, star-shaped particles are excellent.

2. Bulk/film production result

2.1 Mechanical milling method

**Press-formed product**

A cross-sectional photo of the formed and sintered product is shown in Fig.3. The cross-sectional photo of the product whose electric conductivity was measured is shown in Fig.4. Nickel and YSZ are dispersed well. They are not influenced by sintering.

The measurement results of the electric conductivity of the formed product is shown in Fig.5. In all the bulk material, deterioration was found for 100 hours in the initial stage of the measurement, but it is stable at a rate of 600 S/cm or more thereafter. Even though the cross-sectional photos before energization and after energization are observed, the coagulation of nickel is relatively suppressed.

**Plasma spray film**
A cross-sectional photo is shown in Fig.6. In comparison with the existing compound powder, an excellently dispersed state is observed. From the measurement results of the electric conductivity, deterioration of approx. 15% is observed in 500 hours.

2.2 YSZ coating method

Press-formed product

When observed after forming and sintering, the state in which YSZ particles stick to the surface of nickel did not change. However, current hardly flows when the electric conductivity is measured. From the results of the observation, it is estimated that the YSZ coating is hard.

Plasma spray film

From the observation results with EPMA, the dispersion which is better than of the film produced with compound powder is observed (Fig.7). As the measurement result (Fig.8) of electric conductivity show, the electric conductivity is excellent, and tends to become better. Since the dispersion of nickel and YSZ is excellent, the electric conductivity is better than ever. As another reason, it is thought that the amount of YSZ sticking to nickel is less than the initially set amount. The cross-sectionally microscopic observation of the energized product clarifies that the coagulation of nickel is suppressed in comparison with the film which is produced by the existing plasma spray method.

Slurry film

The film production is investigated by using the slurry method with YSZ pellets. A film which is approx. 50 to 100 μm thick can be produced.

CONCLUSION

Mechanical milling method

Raw material powder in which nickel and YSZ are evenly dispersed with the mechanical milling method can be produced.

While the electric conductivity of the press-formed product is stable, the electric conductivity of the product on which film is produced by the plasma spray method is deteriorated.

YSZ coating method

Raw material powder in which nickel is coated with YSZ can be produced.

The method to coat YSZ on the nickel shows an effect to evenly disperse YSZ.
and nickel when film is produced by the plasma spray method in this investigation.

When this method is used in future, the ratio of nickel and YSZ will be fixed. Since the thermal expansion coefficient of nickel does not match that of YSZ, it will be scaled off or cracked. In order to prevent this, making the YSZ amount adjustable will be investigated.

In future, it is planned to manufacture a cell which uses various kinds of powder and to measure the polarization of the fuel electrode.

ACKNOWLEDGMENTS

This research has been executed as entrusted by The New Energy and Industrial Developement Organization (NEDO).

REFERENCE

1. I.Kaji et al. "THE FABRICATION STUDY ON TUBLAR TYPE SOFC APPLIED WITH PLASMA SPRAY COATING", The second International Symposium on SOFC in Athens, Greece (1991), PP221-228.
2. M.Nagata et al. "STUDY ON TUBLER TYPE OF SOLID OXIDE FUEL CELL", The International Fuel Cell Conference in Makuhari, JAPAN (1992), PP305-308.
3. M.Ono et al. "CHARACTERISTICS OF SOFC COMPONENT BY PLASMA SPRAY COATING METHOD", 5th IEA Workshop Julich, Germany (1993), PP303-308.
4. Nakajima et al. "DEVELOPMENT OF SOFC COMPONENTS BY PLASMA AND FLAME SPRAY COATING METHOD", The third International Symposium on SOFC in Honolulu, USA (1993), PP697-704.

Table 1 The production condition of mechanical milling method

| Rotational speed | 2000rpm |
|------------------|---------|
| Treatment time   | 5, 15, 30 min |
| Treatment material | Nickel | YSZ |
| Weight percentages | 60% | 40% |
| Treatment weight | 50g |
Table 2. Several kinds of particles in terms of particles size and shape.

| Number | Shape                        | Size   |
|--------|------------------------------|--------|
| 1      | Spherical shape              | -124 μ m |
| 2      | Spherical shape              | 10-20 μ m |
| 3      | Flake shape                  | -100 μ m |
| 4      | Star shape                   | 3-7 μ m  |
| 5      | Spherical shape (Rough surface) | -60 μ m |
Fig. 2  SEM photo of YSZ coating particle surface.

Fig. 3  The cross-sectional photo of the formed and sintered product.
The cross-sectional photo of the product whose electric conductivity was measured. 

| Time    | Porosity (%) | Pore size (\(\mu\)m) |
|---------|--------------|----------------------|
| 5min    | 42.2         | 1.62                 |
| 15min   | 44.3         | 1.94                 |
| 30min   | 44.4         | 2.07                 |

Fig. 5 The measurement result of the characteristic and electric conductivity of formed product. Nickel powder is 1-2 \(\mu\)m. Measurement method is a four probe dc set up and dc conductivity in air at 1000 °C.
Fig. 6 A cross-section photo of film formed by plasma spray method.

Fig. 8 The measurement result of the electric conductivity of plasma spray film. Treatment time is 10 minutes. Measurement method is a four probe dc setup and dc conductivity in air at 1000 °C.
Fig. 7 EPMA cross-sectional micrograph of plasma spray film.