Characteristics of Electrolyte Processed by CO₂ Laser Evaporation Techniques

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ABSTRACT

The CO₂ laser evaporation (laser PVD) technique was studied to form dense and thin 8 mol% yttria stabilized zirconia (YSZ) electrolyte films. The process parameters for laser PVD were determined on the basis of YSZ physical properties and Al₂O₃ evaporation conditions. Small-size cells of which electrolytes had been made by laser PVD were tested and their performances compared with low pressure plasma spraying, plasma spraying and detonation spraying cells. On the laser PVD cells, highest open circuit voltage and lowest IR drop obtained. A scanning electron microscope study and other characteristics measurements of the electrolyte films suggested laser PVD as one of the best electrolyte forming processes.

1. INTRODUCTION

In order to improve the SOFC performance, we have studied reducing the thickness of the electrolyte and its electric resistance by making dense and thin film of 8 mol% yttria stabilized zirconia (YSZ) by laser evaporation technique.

The CO₂ laser evaporation (laser PVD) technique has been recently developed in our laboratory(1). In this paper, we describe this CO₂ laser technique for dense and thin YSZ electrolyte film formation and compare it with other conventional processes such as plasma spraying, low pressure plasma spraying(2) and detonation spraying. By comparison of I-V characteristics of different fuel cells and physical properties of YSZ films, most desirable process for electrolyte film formation was determined.

2. CO₂ LASER EVAPORATION PROCESS FOR YSZ FILM

As a laser beam does not charge the target material with electricity, evaporation process in a vacuum chamber using the CO₂ laser as heating source has an advantage in comparison with thin film formation methods such as ion plating: it can stably melt and
evaporate the target material. Above all, CO₂ laser beam energy can be easily absorbed on oxides such as YSZ and Al₂O₃ because of CO₂ laser beam length (=10.6μm), resulting in high evaporation rate of oxides as shown in Fig.1.

However, laser beam irradiates the target in the vacuum chamber through a KCl window. Therefore, some amount of deposition on the window is inevitable and the window is more apt to break after absorbing beam energy during PVD processing than the conventional systems. In our laboratory, a special mechanism was devised to prevent the deposition on the KCl window and conduct laser PVD without cracking a window.

Fig.2 illustrates the schematic drawing of the CO₂ laser evaporation technique. Target used consisted of powder, wherein the laser beam was irradiated on the target surface and target received lower laser energy density compared to a solid target, resulting in fairly uniform evaporation of the target material. The composition of the target was not adjusted.

The YSZ film was deposited at a pressure of 5 x 10⁻⁴ Torr. The targets consisting of powder were prepared from YSZ used for plasma spraying without composition adjustment because it did not change after evaporation. The powder size distribution was 10⁻⁴4μm. The target was mounted about 75 mm apart from the substrate which was heated to 450°C during deposition, and irradiated by defocussed CO₂ laser beam (λ=10.6μm) at an incident angle of 12° through a KCl window, on which evaporated particles were prevented from depositing by a suitable technique. The process parameters were determined on the basis of YSZ physical properties and Al₂O₃ evaporation conditions. Table 1 shows laser PVD conditions used for YSZ film formation.

The YSZ electrolyte films deposited by laser PVD were characterized by scanning electron microscope, X-ray diffraction, gas permeability and electrical resistivity. Gas permeability of the coated film was compared by gas leaking rate calculated from leak time at room temperature by means of the apparatus shown in Fig. 3. YSZ film coated on the Ni porous plate was bonded to the steel box A by silicon rubber adhesive and the time of initial N₂ gas pressure (500mmH₂O) changing to 300mmH₂O was measured. Electrical resistivity was also measured by conventional DC fourprobe technique at 500~1000°C. The films formed by other techniques were also characterized in the same manner.

3. PREPARATION OF SMALL-SIZE CELL

Fabrication method of mini-size cell is shown in Fig.4. The porous Al₂O₃ was used as substrate on which Pt mesh(#80) was attached partially by Al₂O₃ cement. Fuel electrodes were formed on the substrate by acetylene gas flame spraying of NiO powder. The electrolytes were formed by plasma spraying, detonation spraying, low pressure plasma spraying and laser PVD. Finally, La(Sr)MnO₃ as air
electrode was coated by acetylene gas flame spraying and connected to the Pt mesh(#80).

4. RESULTS AND CONCLUSIONS

YSZ film composition and structure did not change after laser PVD and spraying. Fig. 5 gives the electric resistances of YSZ electrolytes formed by laser PVD, low pressure plasma spraying and plasma spraying. At 1000°C, only a slight difference of resistivity owing to the film formation technique was observed. Electrical resistivity of YSZ at 1000°C was $\sim 10^2 \Omega \cdot cm$. Gas permeability of SOFC components is presented in Fig. 6. Air electrode formed by flame spraying and fuel electrode formed by plasma spraying were of rather high permeability at the level of $1\sim 10$ cc/sec $\cdot$ cm$^2$. On the other hand, electrolyte should be highly dense and less gas-permeable. YSZ film formed by laser PVD had the lowest permeability of $10^{-3} \sim 10^{-2}$ cc/sec $\cdot$ cm$^2$.

The cells, of which electrolytes were formed by different processes, were tested at $\sim 1000^\circ$C with hydrogen as fuel gas and air as oxidizing gas. Fuel gas flow rate was $\sim 1 \, l/min$. Fig. 7 shows the I-V characteristics of the cells. Open circuit voltage was dependent on the electrolyte forming process. Detonation and plasma spraying cells showed lower OCV values; the highest OCV value was observed in laser PVD cell of which electrolyte was rather dense. IR drop was found to be related to the electrolyte thickness and it was thinnest in laser PVD cell as can be seen in the micro-structure SEM photos of YSZ electrolytes (Fig. 8). Also in Fig. 8, YSZ film formed by plasma spraying has many pores which explain the lower OCV value. Much fewer pores in the low pressure plasma spraying and laser PVD films are consistent with higher OCV values observed in mini-cell test. But detonation spraying cell did not give higher OCV although its SEM photo of YSZ film showed no significant pores. This is thought to be related to several cracks caused by detonation shocks during spraying.

It is concluded that electrolyte made by CO$_2$ laser evaporation technique was highly dense and thin, and CO$_2$ laser evaporation technique is considered the best electrolyte forming process.

REFERENCES

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TABLE I

Deposition condition of YSZ films

| Laser power | 500W         |
|-------------|--------------|
| Target      | YSZ(8mol%Y₂O₃) |
| Pressure    | 10⁻² torr in air |
| Substrate temperature | 450°C     |
| Distance between target and substrate | 75 mm |

Fig. 1 Effect of laser power on deposition rate of oxide film.
Vacuum chamber

CO₂ laser

KCl window

Heater

Substrate

Pumping

Fig. 2 Schematic diagram of CO₂ laser deposition apparatus.

Fig. 3 Measuring apparatus for gas permeability of SOFC components.
Fig. 4 Small-size cell structure.

Fig. 5 Electric resistance of YSZ electrolytes.
Fig. 6 Gas permeability of SOFC components.

Fig. 7 I-V characteristics of small cells.
| Electrolyte Formation Process | Cross Section of Cell |
|-------------------------------|-----------------------|
| Plasma Spray                  | ![Cross Section](image) |
| Low Pressure Plasma Spray     | ![Cross Section](image) |
| LPV+ Laser PVD                | ![Cross Section](image) |
| Detonation Spray              | ![Cross Section](image) |

Fig. 8 Micro-structure of YSZ electrolytes.