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Application of plasma spraying to solid oxide fuel cell production

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Abstract

New technology for electricity generation is required to be efficient, environmentally benign and able to handle a variety of fuels. The solid oxide fuel cell (SOFC) power system could be a promising technology which satisfies all these requirements. Plasma spray technology has become a practical process to produce the coatings for SOFC components. Especially, the low pressure plasma spraying process has been realized to form a dense electrolyte coating of yttria stabilized zirconia. The advantages of plasma spraying technology increase the fuel utilization to 87.1% and the efficiency to 38% in SOFC electric power conversion. On the basis of the ability of cell characteristics achieved by plasma spraying process, a 1kW module has been developed and successfully operated for 3000 hours. The module has been also scaled up to 10kW and is now under operating.

1. Introduction

Energy and the earth environment have become major issues in recent years. Many efforts have focused on the effective use of energy sources and the minimizing effect on the environment. The utilization factor of fossil fuels is approximately 80% and fossil fuels are the most important sources of energy in Japan. From the point of view that about 37% of the total energy consumed is for power generation, the conversion technology of the energies into power generation is recognized as a key technology at present and for the future.

Solid oxide fuel cell (SOFC) has become a promiing technology which is efficient, environmentally benign and able to handle a variety of fossil fuels. SOFC is mainly composed of an electrolyte, electrodes and an interconnector. These components are formed by some processes as coatings[1].

This article shows that the plasma spraying has become one of the most promising processes to produce the SOFC component coatings.

2. Principle and Features of SOFC

Fig.1 shows the operating principles of SOFC. The basic element of SOFC consists of solid oxide electrolyte coating in contact with a porous anode (air electrode) and cathode (fuel electrode) on either side. The fuel and oxidant gases flow past the backside of the anode and cathode, respectively, and generate electrical energy by electrochemical oxidation of fuel, and the electrochemical reduction of oxygen. The transport rate of oxygenions in the solid oxide electrolyte is adequate for practical application at the high temperature of about 1273K.

The cell potential will be decreased from its equilibrium potential of 1.0V at 1273K because of irreversible losses in a practical fuel cell. The losses originate primarily from three sources : (i) ohmic polarization, (ii) concentration polarization and (iii) activation polarization. These losses result in a cell voltage for a fuel cell that is less than its equilibrium potential.

In order to increase the cell performance, the material and its processing for SOFC components are important to decrease the losses.

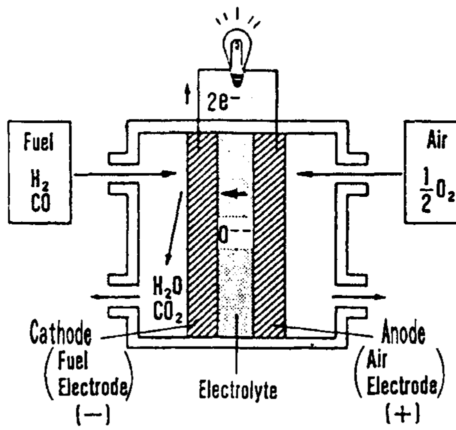

Fig.1 Principle of SOFC.

Table 1 shows the main components of SOFC, the characteristics required for SOFC and examples of applied materials. Since the solid oxide electrolyte is lower in conductivity than other component materials, the increase in conductivity and reduction in resistance by reduction of coating thickness have much effect on the improvement of cell performance. Yttria stabilized zirconia (YSZ) is usually utilized as a solid oxide electrolyte from the aspects of conductivity and economical efficiency. The air electrode material used is lanthanum composite oxide (for example $LaCoO_3$) of perovskite structure, because of its stability and high conductivity in a high temperature oxidizing atmosphere.

As a metallic material is applicable to a fuel electrode in a reducing atmosphere, Ni alloy cermet with YSZ is used. The electrode structure has to be porous to provide an extensive electrode/electrolyte interfacial region for electrochemical reaction and to transport the gaseous reactants.

Table 1 Components of SOFC and required characteristics.

Component	Characteristics	Structure	Materials
Cathode electrode	· High ionic and electronic conductivity · Stable in high temperature oxidizing atmosphere · Thermal expansive characteristic matching with other components	porous	$LaCoO_3$ $LaMnO_3$ $LaSrMnO_3$
Anode electrode	· High electronic conductivity · Stable in high temperature · Thermal expansive characteristic matching with other components	porous	Ni Ni-ZrO_2 Ni-Al_2O_3
Electrolyte	· High ionic conduvtivity and high ionic transport number · Stable in high temperature · No gas permeability	dense	YSZ
Interconnector	· High electronic conductivity · No gas permeability · Stable in high temperature oxidizing and deoxidizing atmosphere	dense	Ni alloy-Al_2O_3 Ni alloy-CSZ $LaCrO_3$
Support tube	· High gas permeability · Electric insulation · Thermal expansive characteristic matching with other components · Low cost	porous	CSZ

Table 2 Production processes for SOFC components.

Classification		Processes	Components
Coating	Thermal spraying	· Plasma spraying · Low pressure plasma spraying · gas flame-spraying	· Electrode · Electrolyte · Interconnector · Protective coating
	CVD	· Electro-chemical vapor deposition · CVD	· Electrolyte · Interconnector
	PVD	· Spattering · Ion plating	· Electrode · Electrolyte
Forming and sintering	Slurry forming	· Slurry coating · Slip coating · Doctor blade	· Electrode · Electrolyte · Interconnector
	Forming with plasticizer	· Extrusion · Injection molding	· Electrolyte · Support tube
	Press forming	· Dry pressing · Hot pressing · Hot isostatic pressing	· Electrolyte · Support tube

In order to equalize the thermal expansion with that of the components of cell, especially the electrolyte of YSZ, calcia stabilized zirconia (CSZ) of porous material is used for a support tube.

Some material processes as shown in Table 2 are tried for the production of the components of cell. Mitsubishi Heavy Industries, LTD. applies the plasma spraying for coating of all the components. The processes as listed in Table 2 have advantages on one hand and disadvantages on the other.

Although the plasma spraying was considered as inappropriate for producing a dense electrolyte coating, the coating corresponding to a sintered layer has become possible lately and its practicability has become high.

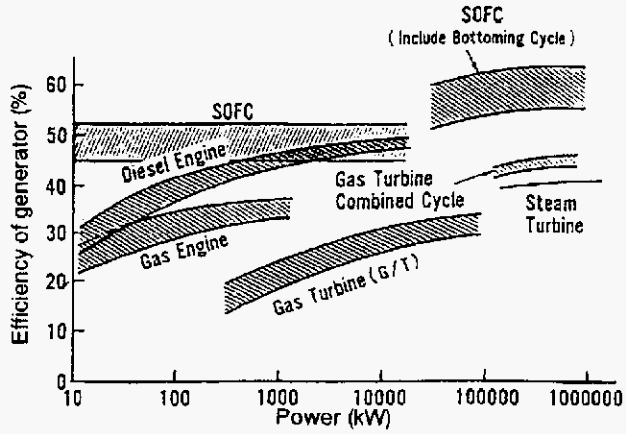

Fig.2 Efficiency of generators.

The SOFC power generator based on aforementioned principles has many favorable characteristics for energy conversion system ; several of these general characteristics are ;

(i) high energy conversion efficiency (Fig.2)
(ii) flexibility in fuel use
(iii) cogeneration capability
(iv) very low chemical and acoustic pollution

3. Application of Plasma Spraying to Cell Production

The structure of SOFC is divided into two types, that is, a tubular type and a planar type, which have been developed for stationary power generation, on-site power generation and mobile power sources. The tubular type SOFC has advanced to near practical use compared to the planar type one[2,3].

Plasma spraying have been applied to the production of tubular type SOFC. Fig.3 shows the tubular type SOFC produced by plasma spraying. The multiple circular-striped cells are formed on a surface of a support tube of about 20mm in diameter (hereinafter referred as cell tube). Fig.4 shows the structure of cell tube's transaxial section. On the support tube are arranged multiple cells composed of such coatings as fuel electrode, electrolyte and air electrode that are directly connected with a interconnector coating. Since the interconnector material is cermet of Ni alloy and Al_2O_3, the Al_2O_3 protective coating for resistance to

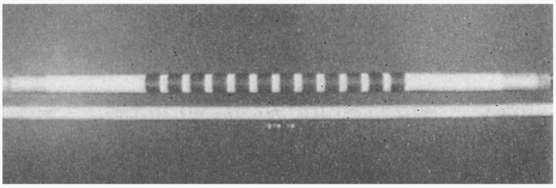
Fig 3 Appearance of tubular type SOFC.

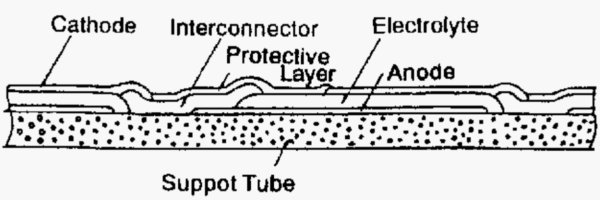

Fig.4 Schematic illustration of a tubular type SOFC.

oxidation is formed on the interconnector coating. The electrolyte coating which requires especially high density is formed by low pressure plasma spraying. The fuel electrode coating made of cermet, interconnector coating and ceramic protective coating are all formed by plasma spraying.

Fig.5 shows the comparison of YSZ coating densities in terms of coefficient of gas permeability. The YSZ coating is formed by the low pressure plasma spraying (LPS) and by atmospheric plasma spraying (APS), actually by changing spray particle diameters. The gas permeability of YSZ coating formed by LPS is lower in value by one digit than that of the coating formed by APS and can be improved further by reducing the spraying particle diameter.The YSZ coating formed by LPS has an advantage of being dense in structure and high in strength. The LPS is an indispensable for cell production. The sectional structure of an cell part with coatings formed by plasma spraying is shown in Fig.6.

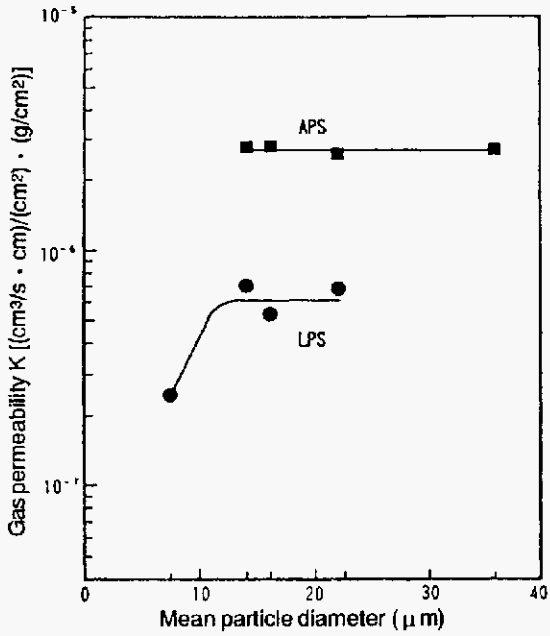

Fig.5 Effect of particle diameter on gas permeability of YSZ plasma sprayed coating.

Each component coatings are adequately formed on the support tube, and the adhesion between them is sound.

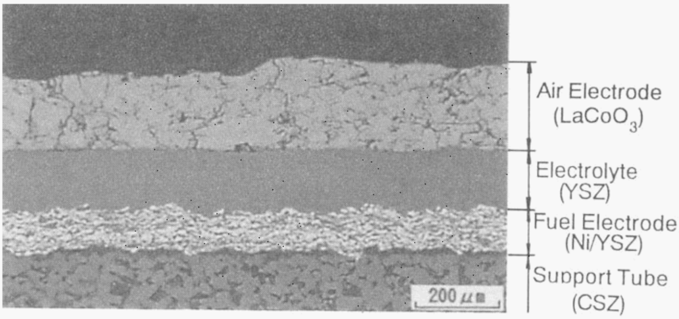

Fig.6 Microstructure of SOFC formed by plasma spraying.

With regard to the interconnector coating, it is necessary to decrease thermal expansion coefficient in relation with the support tube and also reduce thermal stress which occurs in a heat cycle while the SOFC is in operation. Therefore, the interconnector is a composite coating of ceramic and metallic materials which are formed by plasma spraying.

Fig.7 shows the relation between the mixing ratio of Al_2O_3 to Ni alloy and the resistivity of the coating. Even in case the mixing ratio of Al_2O_3 is high, a relatively low resistivity is shown.

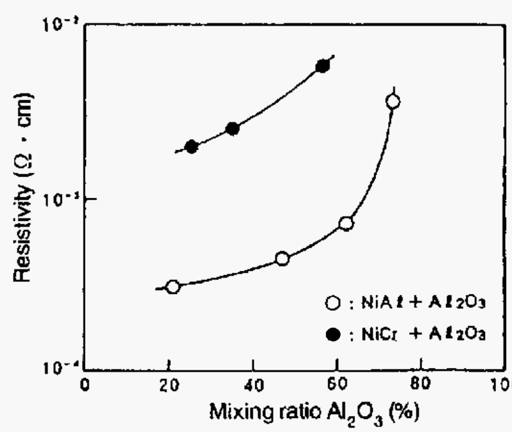

Fig.7 Effect of mixing ratio of Al_2O_3 on resistivity of Ni alloy sprayed coating.

Since the coefficient of linear thermal expansion is proportion to the mixing ratio of metal to ceramics, it is possible to make compatible both the coefficient of linear expansion and conductivity by controlling the mixing ratio of ceramics.

Plasma spraying is applicable to coating formation at a high rate and is also suitable for a wide range of material applications such as coating for SOFC.

4. Cell Performance and kW Module Development

The SOFC performance is determined by a no-load electromotive force and internal resistance, but it is necessary to evaluate its performance by the fuel utilization factor and power generation efficiency for practical use. Fig.8 shows an example of the relation between the fuel utilization factor and the voltage of the cell produced by plasma spray. The fuel utilization is high (87.1%) and the high power generation efficiency (38%) is also obtained.

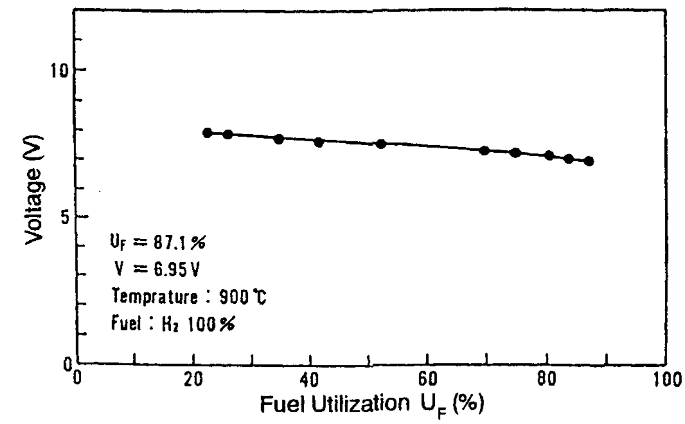

Fig.8 Fuel utilization characteristics.

These high values are achieved by the improvement in the density of the electrolyte coating, in the adhesion between each cell component coatings and in the cell configuration. These facts show that the performance of the tubular type SOFC produced by plasma spraying is excellent and has the high usability.

Fig.9 shows the construction of a 1kW module in which 48 cell tubes are built up. The module consists of a fuel supply chamber, a fuel exhaust chamber, a reaction room and an air preheater. The cell is of a structure hanging from the lower tube plate in the fuel exhaust chamber and free from thermal expansion.

Fuel is distributed from the fuel supply chamber to respective cell tubes, and the steam produced by means of power generation reaction and unutilized fuel are discharged out of the system. On the other hand, air is heated in the air preheater and supplied to the reaction room. The unused air is passed through the air outlet pipe and after being heat-recovered at the air preheater, the air is discharged out of the system. Since the fuel system is independent of the air system, it is possible to use or treat the exhaust gas freely. Therefore, the SOFC is of an excellent construction when viewed from the aspect of a composite system and exhaust gas treatment. The expected performance such as the maximum output of 1.3kW and the rated output of 1.2kW is obtained in this module and it has been confirmed that the change in efficiency is small at a power generation test conducted for 3000 hours. The module has been also scaled up to 10kW with about 500 cell tubes and is now under poerating successfully.

A tubular type SOFC to which the aforementioned plasma spraying has been applied has advanced to near commercialization. The SOFC performance has been actually verified. In order to develope a large capacity module for commercial use, it is necessary to increase the cell production efficiency and to reduce the production cost. To this end, plasma spray materials and plasma spraying technology are required to be further improved.

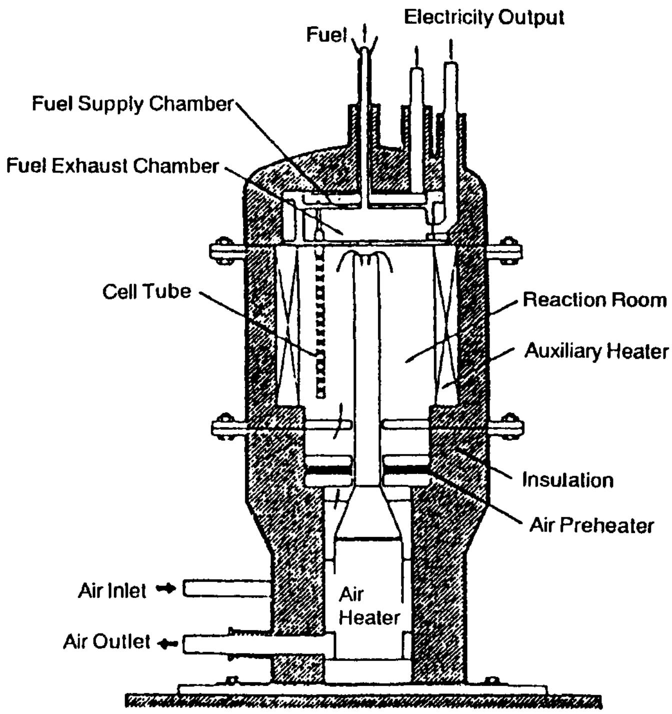

Fig.9 Construction of 1kW SOFC module.

5. Conclusion

Applying plasma spraying to tubular type SOFC has realized excellent performance such as high fuel utilization factor of 87.1% and high power generation efficiency of 38%. These advantage are achieved by improvement of plasma spraying technology in the density of the electrolyte coating, in the adhesion between each cell component coatings and in the cell configuration.

A 1kW module has been developed, which is fabricated by assembling 48 cell tubes, and has successfully operated for 3000 hours. The module has been also scaled up to 10kW and is now under operating.

The larger module for commercial use is to be developed by improving the productivity and economy.

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