

## 이동형 연료전지용 마이크로 채널 개질기 제작

유상필<sup>†</sup>, 임성대\*, 이원교\*\*, 김창수\*  
\*한국에너지기술연구원 고분자연료전지연구단  
\*\*연세대학교 화학공학과

## Fabrication of Microchanneled Reformer for Portable Fuel Cell

S.P. Yu<sup>†</sup>, S.D. Lim\*, W.K. Lee\*\* and C.S. Kim\*

\*PEFC Research Department, Korea Institute of Energy Research, 71-2 Jang-dong,  
Yuseong-Gu, Deajeon, 305-343, Korea

\*\*Chemical Engineering department, Yonsei Univ., 134 Seodeamoon-Gu,  
Seoul, 120-749, Korea

### ABSTRACT

소형 PEMFC(Proton Exchange Membrane Fuel Cell)는 전기를 만들기 위해서 고순도의 수소를 필요로 한다. 각각의 마이크로 성형된 금속박판(스테인레스 스틸, 알루미늄)을 진공 브레이징법으로 접합하여 수소공급용 소형 개질기를 제작하였다. 마이크로 채널의 내부는 졸-겔법(스테인레스 스틸)과 양극산화법(알루미늄)으로 촉매를 지지하기 위한 다공성 Al<sub>2</sub>O<sub>3</sub> 층을 형성시켰다. 스테인레스 스틸 박판은 에칭과 브레이징에 유리하였으나, 표면 산화층 코팅을 균일하게 하여 안정적인 촉매반응을 유도하기 위한 균일한 표면 산화층 형성이 힘들었다. 반면 알루미늄 박판은 표면 산화층 형성이 상대적으로 용이했으며, 촉매를 상하지 않는 낮은 온도에서의 적층이 가능했다.

**주요기술용어** : Microchanneled Reformer(마이크로 채널 개질기), Fuel Cell(연료전지), Anodizing(양극 산화), Brazing(브레이징)

### 1. INTRODUCTION

The complete reformer-fuel cell unit can be considered as an alternative to conventional sources of electricity such as batteries for

<sup>†</sup> Corresponding author : spyu@kier.re.kr

laptop computers and mobile phones due to its ability to provide an uninterrupted supply of electricity as long as a supply of methanol and water can be provided. The micro reformer-fuel cell combination has the advantage of not requiring the tedious recharging cycles needed by conventional rechargeable lithium-ion batteries. Also, the energy storage density per

unit volume/weight of this system is higher than that of batteries, which translates into less frequent 'recharging' through the refilling of methanol fuel.

Microchannel reformer is an essential component to supply hydrogen to proton exchange membrane (PEM) fuel cells without high pressure H<sub>2</sub> tank.

Catalytic steam reforming of methanol was usually performed as a method of H<sub>2</sub> gas generating reaction. Inner walls of microchannels is coated with catalyst which can burn methanol to generate heat for steam reforming and perform steam reforming with MeOH.

Through microchanneled reformer, the heat of combustion is transferred to steam reforming process. The microchanneled reformer has been made of mechanically microstructured metal foils of stainless steel, hastelloy, aluminum, copper, palladium, silver, and others<sup>1)</sup>. A reactor is assembled from individual metal plates with micro channels having cross sections in the range of 50 - 300  $\mu\text{m}$ . These metal plates are assembled by bolting, gaskets such as graphite or diffusion bonding. Brazing is employed to connect the parent metals : a filler metal, such as Nickel based alloys, is placed, for example in a foil form, between the parts to be brazed and heated upon its melting point. It allows to create tight chemical bonds between parts. Contrary to welding, parent parts are not melted. Below 450°C, brazing is called soldering. After brazing, there are little deformation and residual stresses in the parent metal which is not melted. Moreover, using metal as a bond, joints are tight and heat conductivity between the parent metals is higher than using graphite or polymer as a bond. On the other hand, for a wider application with chemical reactions it is

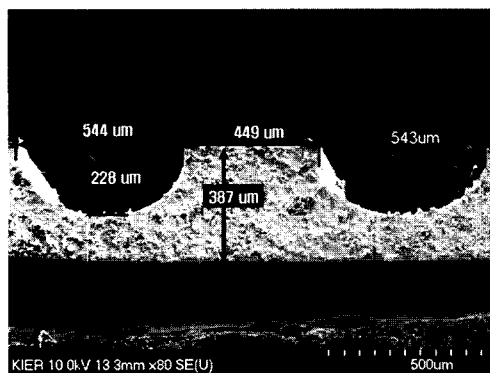
necessary to provide oxide coatings as carriers for metal catalysts to increase the overall inner surface area of the microchannels<sup>1)</sup>. Catalytic coatings are important in microstructured reactors, since they can minimize mass transfer resistance and pressure drop, and improve heat conduction for catalytic reactions. Several techniques have been utilized for coating microchannels with porous oxides: anodic oxidation which has been used to provide a porous layer on aluminum<sup>2,3)</sup>; chemical vapor deposition<sup>4)</sup>; deposition of nanoparticles<sup>5)</sup>; and sol-gel process<sup>1)</sup>. In these coating processes, sol-gel is relatively simple to use and compatible to various kind of metals, but the uniformity and adhesion of coating layers are weak. Anodizing leads to formation of unbranched, regular and nearly concentric pores, which is advantageous for catalytic reactions<sup>6)</sup>. Moreover, the strength of adhesion of the anodic oxide layer to the support is strong. But it can only be applied to aluminum and not stainless steel. In applying catalytic reaction to micro system, fabrication and coating to support catalysts are correlated with each other because the manufacturing process is dependent mutually. This study introduces vacuum brazing technique for assembly of microchanneled stainless steel. It is also attempted to anodize aluminum foil.

## 2. EXPERIMENTS

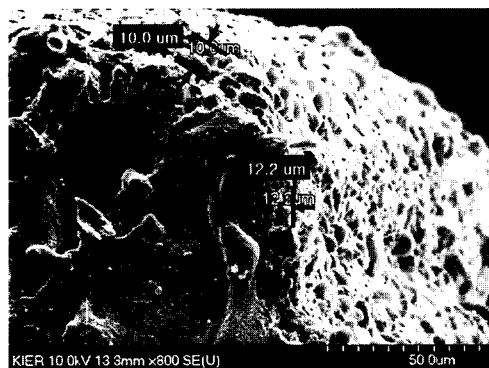
In the design of the micro heat exchanger, uniformity in fluid velocity distribution was considered, referring to Commenge et al<sup>7)</sup>. Main design factors were curvature ratio at the end of microchannels, ratio of depth to width in microchannels, a number of microchannels,



(a) Micro channel patterned plate



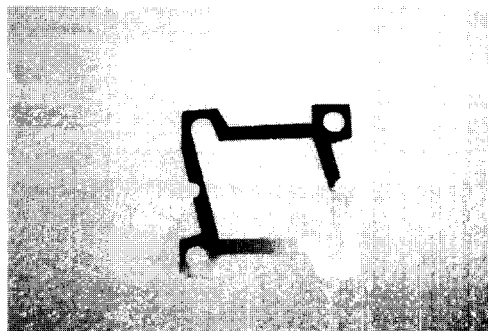
(b) Cross-sectional view



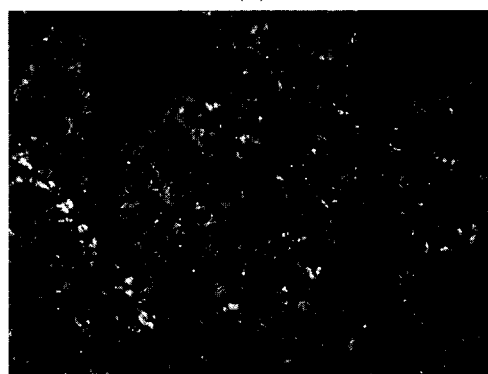
(c) Al<sub>2</sub>O<sub>3</sub> coated channel

Fig. 1 SEM images of microchanneled plate.

length of microchannels and area ratio of wall to microchannels. Top and bottom covers were prepared by machining in 4 × 4 cm<sup>2</sup> of size.



(a)



(b)

Fig. 2 The shapes of filler metal sheets and cross section at each brazing case. (a) nickel foil, thickness: 38μm, width 3.5mm (b) Cross section of brazed stack (×100).

The name of stainless steel plate was SUS304 and that of aluminum plate was AL1050.

Microchannels were created by photolithography and chemical etchings and the details for microchanneled plates are like these; Foil geometry is 40 × 60 × 0.5 mm<sup>3</sup>. Microchanneled area of foil is 30×40 mm<sup>2</sup>. Cross-sectional area of microchannel is 400×230 m. Number of channels a plate is 40.

Microchanneled foil is shown in Figure 1. The shapes of filler metal sheets are shown in Figure 2. The thickness of nickel foils was 38μm, and the width of them were ranged from 2.5mm to plate edge. At each case, the room

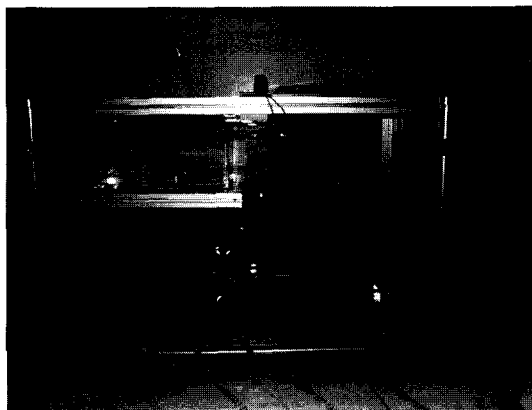


Fig. 3 Aluminum foil anodizing equipment.

between layers of brazed stack was different. If there are impurities on the surface of the parent metal, adhesion force of brazing can be diminished. Therefore, the surface of the parent metal was degreased by alcohol before brazing. Vacuum brazing lasted for 15 minutes at 1000°C, below 10–5 torr. The assembled microchanneled plates were tested for leakage with a leak detector (ASM 142, Alcatel). Leakage tests were performed in ambient air firstly, and then in latex globe filled with helium gas.

For incorporation of catalysts, a microchanneled stainless steel plate was coated with aluminum oxide films by dip-coating with alumina sol, followed by drying in air at 120°C overnight. Alumina coated stainless steel plates were brazed under vacuum with nickel filler metal. On the other hand, microchannels in assembled stainless steel plates were coated by flowing alumina sol followed by blowing excess alumina sol with compressed air and then drying in air at 120°C overnight.

The microchanneled aluminum foils were rinsed with ethanol and deionised water and then dried with compressed air. The electrode was immersed in 165 g/l H<sub>2</sub>SO<sub>4</sub> solution which



Fig. 4 Reactor integrated with microchannel plate.

was circulated with a pump to remove heat generated during anodizing. For constant current operation, the current desired was set on a power supply. Anodizing time was varied from 10 to 30 min. The anodized aluminum foils were washed with deionized water followed by drying in air at room temperature.

### 3. RESULTS AND DISCUSSIONS

Microchanneled stainless steel plate and assembly of microchanneled stainless steel plates are shown in Figure 4. The assembly of microchanneled stainless steel plates was tested for leakage in air and helium environments. Leaking rates are  $3.3 \times 10^{-10}$  torr l/sec and  $1.5 \times 10^{-6}$  torr l/sec in air and helium environments, respectively. Considering that Swagelok fittings are utilized below  $1 \times 10^{-6}$  torr l/sec, our results might be caused by leaking from the fittings rather than from gaps between brazed plates.

In order to examine brazed plates, the assembly of microchanneled stainless steel plates was cut by wire-cutting method. Figure 5 shows both the cross sections and the brazed

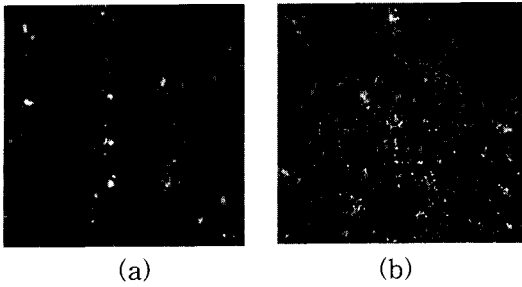


Fig. 5 Photographs of (a) cross section and (b) brazed part of assembly of microchanneled stainless steel plates.

part of the assembly of microchanneled stainless steel plates. The microchannel shape is not rectangular but hemi-circular due to using photo-etchings. It is known that the amount of filler metals is important at brazing technology, as excess filler metals could block microchannels and lack filler metal could cause leaking. In our case, appropriate amount of filler metals was found by varying thickness and width of filler metals. Thus, no gaps are observed between brazed stainless steel plates (see Figure 5(b)). In the microchanneled stainless steel plates brazed and then coated with alumina, SEM picture shows that 3  $\mu\text{m}$  of

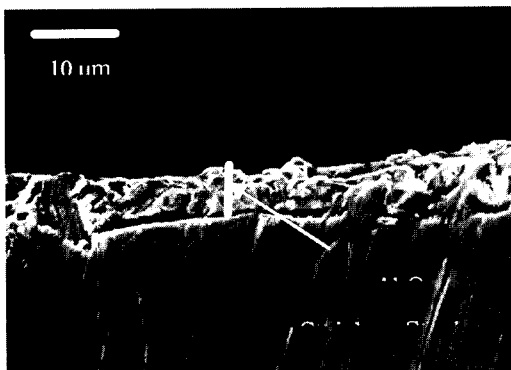
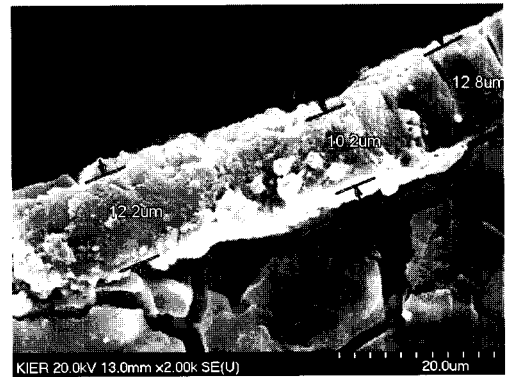


Fig. 6 SEM picture of microchanneled stainless steel plates brazed and then coated with alumina.



(a)

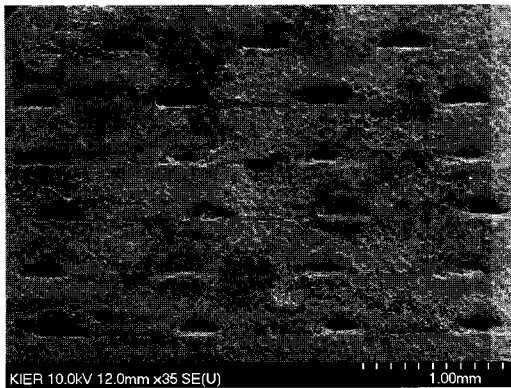


(b)

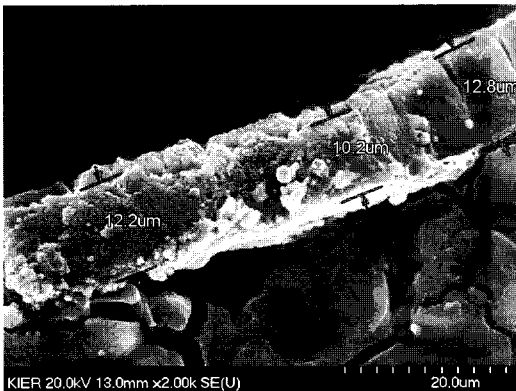
Fig. 7 SEM picture of microchanneled aluminum foils. (a) cross sectional view of microchannel (b)uniform thickness of oxide layer.

alumina film is successfully incorporated onto the microchannels (see Figure 6).

Aluminum foils were anodized and observed with SEM. Aluminum is etched isotropically more than stainless steel (Figure 7(a)). So the cross section of aluminum has more elliptical form. Contrast to sol-gel method in stainless steel, uniform thickness (about 10  $\mu\text{m}$ ) of oxide layer was formed on the surface of aluminum foil (Figure 7(b)). If we vary the density of current or solution, the thickness of oxide layer can be controlled easily. Also mask can provide selective area to be anodized.



(a)



(b)

Fig. 8 SEM pictures of microchanneled aluminum foil stack. (a)Cross sectional view of stack (vertical to microchannel) (b)Cross sectional view of stack.(longitudinal to microchannel).

Anodized microchanneled aluminum foils were stacked and brazed(Figure 8(a)(b)). When brazing method was in process, the foils were floated on the filler metal(melting metal). So the alignment of foil was a critical issue to prevent leakage of the stack. Also optimum amount of filler metal should be deposited because flooding of filler metal could block up the microchannels.

#### 4. CONCLUSION

Microstructured stainless steel plates were etched and brazed with nickel filler under vacuum. The surfaces of the microchannels were coated with Pt/Al<sub>2</sub>O<sub>3</sub> layer by sol-gel method successfully. Alternatively, microchanneled aluminum foil was anodized to make Al<sub>2</sub>O<sub>3</sub> layer for supporting catalyst and then stacked by brazing method. Aluminum foil was good to control oxide film on the surface and stack at low temperature which can avoid catalyst degradation.

#### REFERENCES

- 1) K. Haas-Santo, O. Gorke, P. Pfeifer, K. Schubert, *Chimia*, Vol. 56, No. 11, 2002, pp. 605-610.
- 2) G. Wießmeier, K. Schubert, D. Hönicke, 1997, in *Proceedings of the 1st International Conference on Microreaction Technology*, pp. 20-26, Springer, Berlin.
- 3) R. Wunsch, M. Fichtner, K. Schubert, 6-10 March 2000, in *Proceedings of the 4th International Conference on Microreaction Technology*, pp. 481-487, Atlanta.
- 4) M. Janicke, H. Kestenbaum, U. Hagendorf, F. Schüth, M. Fichtner, K. Schubert, *J. Catal.* Vol. 192, 2000, pp. 282-293.
- 5) P. Pfeifer, M. Fichtner, K. Schubert, M. Liauw, G. Emig, 19-21 April 1999, Frankfurt, in *Proceedings of the 3rd International Conference on Microreaction Technology*, pp. 372-382.
- 6) G. Wießmeier, D. Hönicke, *J. Micromech. Microeng.* Vol. 6, 1996, p. 285.
- 7) J. M. Commenge, L. Falk, J. P. Corriu and M. Matlosz, *AIChE Journal*, Vol. 48, 2002, pp. 345-358.