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Thermally Stabilized Porous Nickel Support of Palladium Based Alloy Membrane for High Temperature Hydrogen Separation

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Nickel powder was coated with aluminum nitrate solution to increase the thermal stability of a porous nickel support and control the nickel content in the Pd-Cu-Ni ternary alloyed membrane. Raw nickel powder and alumina coated nickel powder were uniaxialy pressed by home made press with metal cylindrical mold. Though the used nickel powder prepared by pulsed wire evaporation (PWE) method has a good thermal stability, the porous nickel support was too much sintered and the pores of porous nickel support was plugged at high temperature (over 800℃) making it not suitable for the porous support of a palladium based composite membrane. In order to overcome this problem, the nickel powder was coated by alumina and alumina modified porous nickel support resists up to 1000℃ without pore destruction. Furthermore, the compositions of Pd-Cu-Ni ternary alloy membrane prepared by magnetron sputtering and Cu-reflow could be controlled by not only Cu-reflow temperature but also alumina coating amount. SEM analysis and mercury porosimeter analysis evidenced that the alumina coated on the surface of nickel powder interrupted nickel sintering.

Keywords *: Hydrogen; Membrane; Palladium; Nickel Porous Support; Separation*

1. Introduction

Pd and Pd-alloyed membrane command great attentions for their theoretically infinite hydrogen selectivity, their high hydrogen permeability, and their chemical compatibility with hydrocarbon containing gas streams. Because of these kinds of merits, Pd-based membranes have great possibility of real industrialization compared with any other hydrogen-selective membranes.[1)-4)] Furthermore, utilization of composite structures reduces a material cost as well as offers high hydrogen permeation rate because ultra thin membrane film can be prepared. For high quality of metallic composite membrane support should be highly porous, smooth facial, highly permeable, thermally stable and metallic adhesive and have defect-free surface. Moreover, in order to produce in large quantity of membrane, the manufacturing process should be as simple as possible. Variety of porous supports has been used for palladium-based alloy membranes.

The materials having been commercially used for supports are ceramics, glass and stainless steel. Among the supports, non-metal such as ceramic and glass has smooth surface and good thermal stability. However, it has week adhesion to metallic thin film and lack of mechanical stability to seal into commercial component.[5)-9)] In this regard, porous stainless steel support has been used to improve mechanical strength of the support. From the viewpoint of a practical application, porous stainless steel has the merit of getting more readily sealed into a commercial unit. However, atomic interdiffusion of metals between the thin Pd/Pd alloy layer and the stainless steel components occur during high temperature processing. To inhibit the atomic interdiffusion, diffusion barrier have to be introduced.[10)-15)] Furthermore, the surface roughness and the big surface pore size of the commercial porous stainless steel in comparison with ceramic substrate were tough obstacles for the preparation of thin and pinhole-free Pd-based membrane on it. In order to solve these problems, some methods such as shot peening with iron particles,[16)] polishing,[17)] and deposition of thin metal and/or ceramic layer were reported.[14),18)] However, in spite of those efforts, Pd/PSS membrane still needs many works to be done for its real industrialization. Recently, micro-fabricated silicon wafer[19)] and micro-fabricated nickel [20)] were reported. How-

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ever, the micro-fabrication method is so costly process that high manufacturing cost has to overcome before real industrialization. Furthermore, very narrow effective area of Pd/Ni membrane prepared by microfabrication technology has to be conquered to increase the hydrogen permeability.

In previous papers, we showed a porous nickel support prepared by uniaxial pressing of nickel powder.[21),22)] The pressing process of nickel powder is so simple and reasonable that mass production is possible. And its very smooth surface makes possible to make pinhole-free-Pd-based membrane without pretreatment to make smooth surface. As for a metal substrate, it can offer simplicity for the module construction and overcome the obstacles of ceramic support such as the poor compatibility between the ceramic substrate and the thin Pd-based layer, lack mechanical stability, and the discrepancy of the thermal expansion coefficients between the top Pd-based layer and the substrate causing defect and physical peeling during the temperature changing cycles. However, one particularly significant technical challenge is the development of hydrogen separation membrane that can withstand several operating conditions of high temperatures and high pressure. Because porous nickel support is made of nano size nickel powder, it is too much sintered at high temperature (over 800℃) making poor pore and rough surface. The temperature conditions of typical catalytic gasification and methane steam reforming process are up to 1000 ℃ and 800 ℃ respectively.[23),26)] For economic process configuration, a membrane should be capable for in situ use in separation of hydrogen at elevated temperature without cooling the feed stream temperature. This paper focuses on the increase of thermal stability of porous nickel support of metallic composite membrane and the control of the composition of Pd-Cu-Ni ternary alloyed membrane. In order to increase the thermal resistance of porous nickel support and to control the composition of Pd-Cu-Ni ternary membrane, the nickel powder was coated with aluminum nitrate solution. The raw nickel powder and alumina coated nickel powder was compressed in the cylindrical metal mold at 330 MPa and than treated at the temperature 650-900 ℃ and 900-1000 ℃ respectively under hydrogen condition. The magnetron sputtering of Pd and Cu followed by Cu-reflow to be pinholes free dense membrane was carried out. The membranes were characterized by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and mercury porosimeter

Table 1. The fabrication conditions of porous nickel and alumina modified nickel support.

Filter	Fabrication Pressure [MPa]	Heat Treatment Temp. [℃]	Pretreatment
S650	330	650	Non
S700	330	700	Non
S750	330	750	Non
S800	330	800	Non
S900	330	900	Non
A05S900	330	900	Alumina coating [0.5wt. %]
A05S1000	330	1000	Alumina coating [0.5wt. %]
A10S1000	330	1000	Alumina coating [1.0wt. %]

2. Experimental

2.1 Fabrication of porous nickel and alumina modified nickel support

A nickel powder which has purity of 99.9% made by pulsed wire evaporation (PWE) method having broad particle size distribution from 20 to 5,000 nm was coated with aluminum nitrate solution by incipient wetness impregnation method. Appropriate amount of aluminum nitrate ($Al(NO_3)39H_2O$, Aldrich) was dissolved in deionized water, and the solution added to the dried nickel powder to obtain 0.5 and 1.0 wt.% Al. The alumina modified nickel powder was then dried in a convection oven (120 ℃) for 4 hours and calcined at 400 ℃ for 4 hours. The raw nickel powder and alumina modified nickel powder were compressed without binder in metal cylindrical mold with 50 mm in diameter using a home made press under pressure of 330 MPa. The amount of nickel powder was 20 g for each supports. The compressed porous nickel and alumina modified nickel support were further treated at the temperature 650-900℃ and 900-1000℃ respectively under H_2 condition for 10 hours. It will help the support have mechanical strength and thermal stability. The fabrication conditions of each supports are in Table 1.

2.2 Fabrication of Pd-Cu-Ni ternary alloyed membrane

To increase the adhesion and activation of the support, the surface was treated by H_2/Ar plasma surface modification. After H_2/Ar plasma treatment, Pd was sputtered at 42 W (350V, 120mA) for 40 min followed by Cu-sputtering at 18 W (600V, 30mA) for 10 min. Subsequently, Cu-reflow and Pd-Cu-Ni alloy formation was performed at 700 ℃ for 2 hours. Previous studies[21),22)] show the details of the H_2/Ar plasma surface modification, sputtering and Cu-reflow technique.

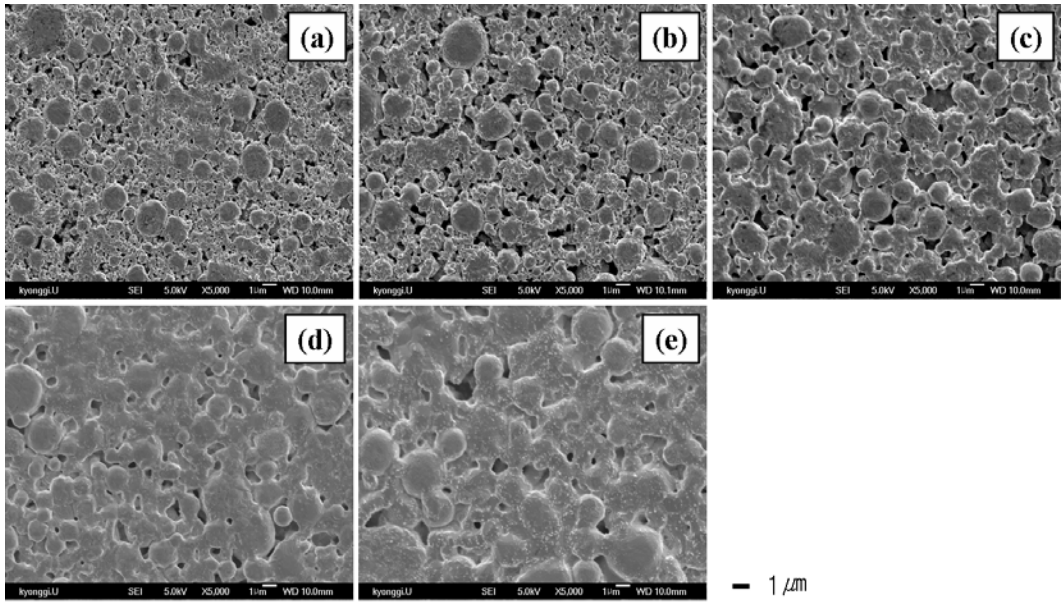

Fig. 1. The SEM images of porous nickel support treated at different temperature: (a) us S650; (b) is S700; (c) is S750; (d) is S800; and (e) is S900.

2.3 Permeation measurements

Permeation test was conducted with single gas of hydrogen at room temperatures and at transmembrane pressure differences of 0.034 to 0.101 MPa. The permeation apparatus consists of a membrane cell, pressure gauge/controller and mass flow controller as shown in previous papers.[21), 22)] Gas was introduced by mass flow controller (MCF, Brooks 5850 E series) and transmembrane pressure difference was regulated by pressure controller (Alicat PC-30PSIG-D). The permeation rate of hydrogen was measured by a digital soap-bubble flow meter. The prepared support was inserted in the membrane cell and tightened to the cell by Viton-O ring.

2.4 Characterization of porous nickel and alumina modified nickel support

The scanning electron microscopy (SEM) was used to characterize the surface of the prepared support and Pd alloy membrane. Pore size distribution, average pore size, total pore volume and porosity of the prepared support were measured by mercury porosimeter (Micromeritics, Autopore Ⅳ 9500). The composition of the metal elements was detected by energy dispersive spectroscopy (EDS).

3. Results and discussions

3.1 Porous nickel and alumina modified nickel support

In previous study, the porous nickel support with diameter of 50 mm and average pore diameter of 33 nm was successfully fabricated and defect-free Pd-Cu-Ni ternary alloyed membrane of 4 ㎛ thickness was deposited without any pretreatment of the support to reduce the pore diameter and roughness.[21)] In order to clarify the effect of heat treatment temperature, S series porous nickel supports were treated at the temperature range of 650-900 ℃ in hydrogen. Fig. 1 shows the SEM images of S series porous nickel support. Since the sintering of raw nickel powder took place from 750 ℃ (S750), the pore fraction drastically decreased with rising the heat treatment temperature. Above 800 ℃ (S800), the great part of the support melted down and the most of pores were plugged.

For the wide application such as high temperature operation it needs to increase the thermal resistance of the porous nickel support. In this regard, the porous nickel support had been modified by alumina coating. As shown in Fig. 2, i.e. the EDS analysis of porous nickel support (a) and alumina modified porous nickel support (b), alumina was well coated on nickel powder by incipient wetness impregnation method. Fig. 3 shows the SEM images of alumina modified porous nickel support. (a) and (b) in Fig. 3 were for those coated with 0.5 wt.% of alumina and treated at 900 ℃ and 1000 ℃ respectively. (c) is for the one coated with 1.0 wt.% of alumina and treated at 1000 ℃. As shown in Fig. 3, A05S series supports show very stable structure up to 900 ℃ (A05S900). At 1000 ℃ (A05S1000), the powder melted down and some pores were plugged. On the other hand, A10S1000 which was coated with 1.0 wt. % of alumina and treated at 1000 ℃

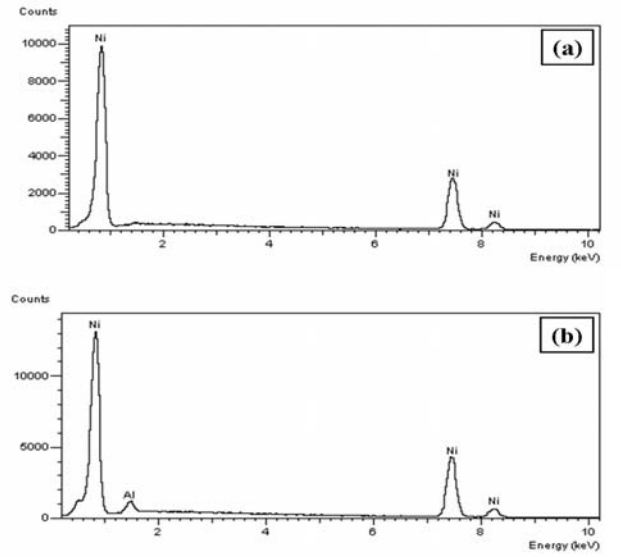

Fig. 2. EDS analysis of porous nickel support and alumina modified porous nickel support: (a) is S700; and (b) is A10S1000.

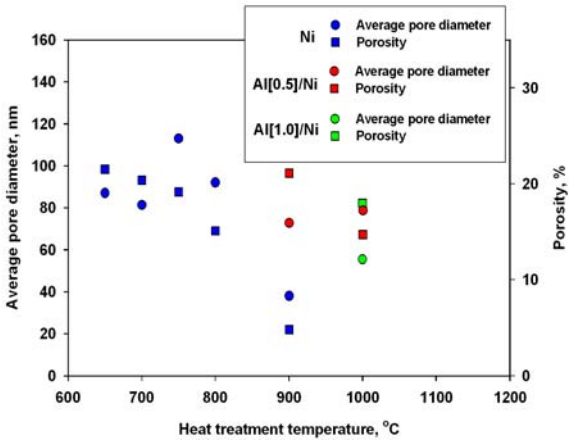

Fig. 4. The effect of heat treatment temperature on the average pore diameter and the porosity of porous nickel support and alumina modified porous nickel support.

has very stable pore structure there being little indications of nickel powder melting down and pore plugging.

Average pore diameter and porosity are indications of melting down of nickel powder and plugging of pores. As shown in Fig. 4, average pore diameter was larger than that of previous study.[21] The reason will be explained in the following section. The porosities of S series supports decreased with increasing heat treatment temperature. On the other hand, the average pore diameters of S series supports increased with an increase of heat treatment temperature from 700 to 750 ℃ and then decreased with increasing heat treatment temperature. The surface sintering of nickel powder at 750 ℃ extends the pore size and it seems to cause the increase of average pore diameter. However, above 750 ℃, nickel powder was sintered and the pores were plugged leading the decrease of porosity and average pore diameter. On the other hand, the porosities of A05S series supports coated with alumina of 0.5 wt. % decreased with increasing heat treatment temperature and the average pore diameters of those increased with heat treatment temperature from 900 to 1000 ℃. Porosity and average pore diameter of A05S900 support treated at 900 ℃ were similar to those of S700 support fabricated with raw material and treated at 700 ℃. While porosity of A10S1000 support coated with 1.0 wt. % of alumina and than treated at 1000 ℃ was similar to that of S750 fabricated with raw material and treated at 700 ℃, average pore diameter was less than those of S series supports treated from 650 ℃ to 800 ℃. The reason is not clear but we suppose that alumina coated on the nickel powder may decrease average pore diameter. Uemiya[27] suggested that relations between the thickness of Pd layer and pore size were 13 ㎛ in thickness vs. 0.3 ㎛ in pore size, 4.5 ㎛ vs. 0.2 ㎛, 2.2 ㎛ vs. 0.1㎛ and 0.8 ㎛ vs. 5 nm. Since the average pore diameter of all prepared support but S750 are smaller than 100 nm, we hope that ultra-thin membrane film down to 2 ㎛ can be deposited.

Fig. 5 shows the total pore volumes of S, A05S and A10S series support. Total pore volumes also were af

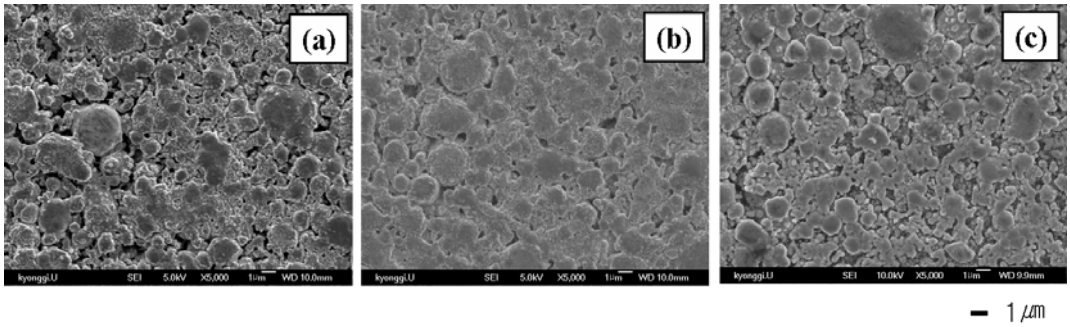

Fig. 3. The SEM images of alumina modified porous nickel support: (a) is A05S900; (b) is A05S1000; and (c) is A10S1000.

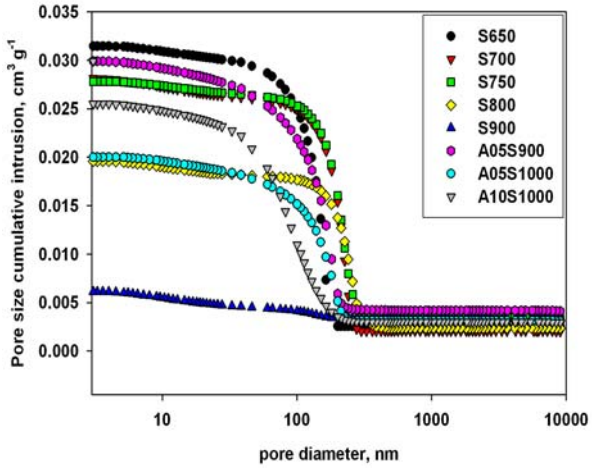

Fig. 5. The total pore volume of porous nickel support and alumina modified porous nickel support.

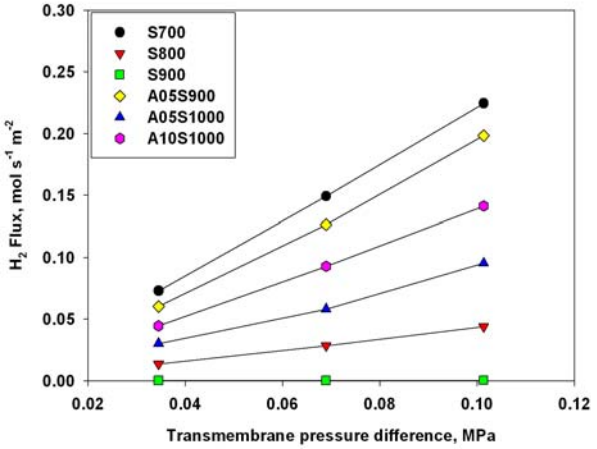

Fig. 6. The hydrogen permeation flux via transmembrane pressure difference of porous nickel support and alumina modified porous nickel support.

fected by heat treatment temperature. The total pore volumes of S650, S700 and S750 supports fabricated with raw material terial and treated at 650 ℃, 700 ℃ and 750 ℃ respectively were similar to each other. It means that S series support thermally withstands up to 750 ℃. A05S900 coated with 0.5 wt. % of alumina and than treated at 900 ℃ was similar to those of S650, S700 and S750. It means that the A05S series supports thermally withstand up to 900 ℃ while S series supports thermally withstand up to 750 ℃. Furthermore, alumina coating amount also has an effect on thermal stability. As shown in Fig. 5, total pore volumes of A05S1000 and A10S1000 treated at 1000 ℃ increased from 0.02 cm^3 g^{-1} to 0.025 cm^3 g^{-1} with increasing alumina coating amount from 0.5 wt. % to 1.0 wt. %.

From SEM and mercury porosimeter analysis, it can be insisted that not only alumina coating on the surface of nickel powder prohibit nickel sintering, melting down, and pore plugging but also alumina coating amount increase the thermal stability.

3.2 Hydrogen permeation test

In Fig. 6, the hydrogen permeations of S, A05S and A10S series support were shown as a function of pressure drop. The test was carried out at room temperature. As shown in Fig. 6, the hydrogen permeations linearly increased with increasing pressure drop. The increasing rates of hydrogen permeation (slops of graph) of S series support drastically decreased at the heat treatment temperature of 800 ℃. The hydrogen permeation of S900, treated at 900 ℃, was almost naught. On the other hand, the hydrogen permeation flux of A05S900 which was coated with 0.5 wt. % of alumina and treated at 900 ℃ was similar to that of S700. The hydrogen permeation flux of A10S1000 which was coated with 1.0 wt. % of alumina and treated at 1000 ℃ was higher than that of A05S1000 which was coated with alumina of 0.5 wt. % and treated at 1000 ℃ and less than that of A05S900 because the average pore diameter of A10S1000 was smaller than A05S900. However the hydrogen permeation flux of A05S1000 was much higher than the previous results where the gas permeation was contributed by Knudsen diffusion.[21] We have to increase the hydrogen permeation flux of porous nickel support because it caused support resistance on hydrogen permeation in Pd-Cu-Ni ternary alloy membrane.[28] For this reason we choose another nickel powder in which the portion of micron-sized powder was larger than that of previous study. It helps the average pore diameter and hydrogen permeation flux of the support increase.

3.3 Pd-Cu-Ni ternary alloyed membrane

Porous nickel support was modified with alumina coating on a nickel powder and it means that it can have problems such as the week adhesion and different thermal expansion coefficients between membrane film and support which took place in porous alumina and porous glass.[5),7),29] In order to clarify the effect of alumina coating on a nickel powder, we deposited Pd and Cu film by sputtering followed by Cu-reflow.[22),30] As shown in Table 2, the films were Pd-Cu-Ni ternary alloyed membrane. It means that the adhesion between membrane film and porous support may be so good that there will not be problems taking place in porous alumina and porous glass. The surface and cross-section SEM images of Pd-Cu-Ni ternary membrane deposited on the three different supports are in Fig. 7. We can see defect-free surfaces of membrane films and the film thickness of three different kinds of membrane

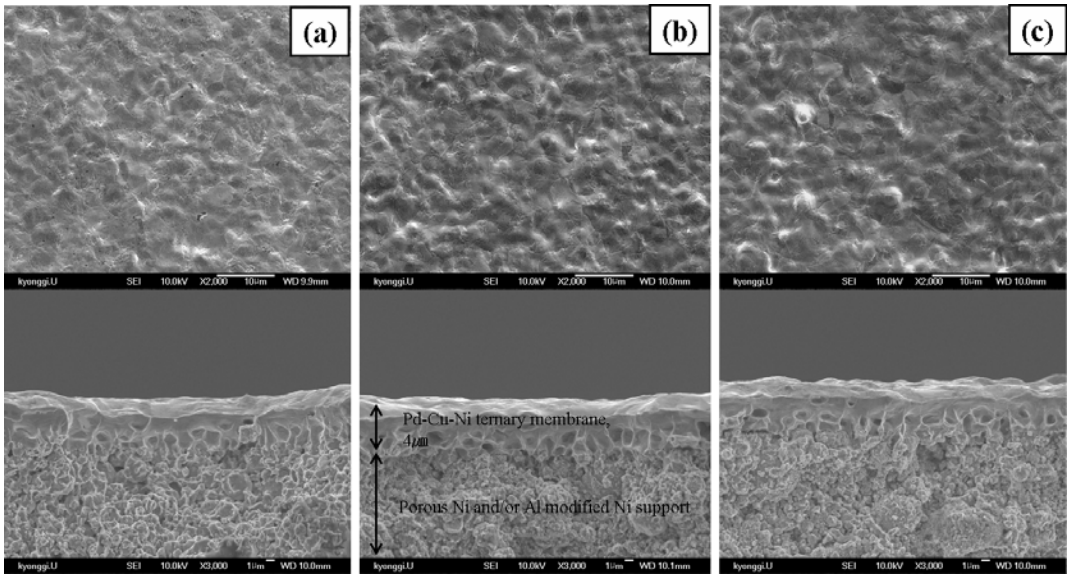

Fig. 7. The surface and cross section SEM images of Pd-Cu-Ni ternary alloy membranes deposited on an porous nickel support and alumina modified porous nickel supports: the support are S700(a), A05S900(b), and A10S1000(c).

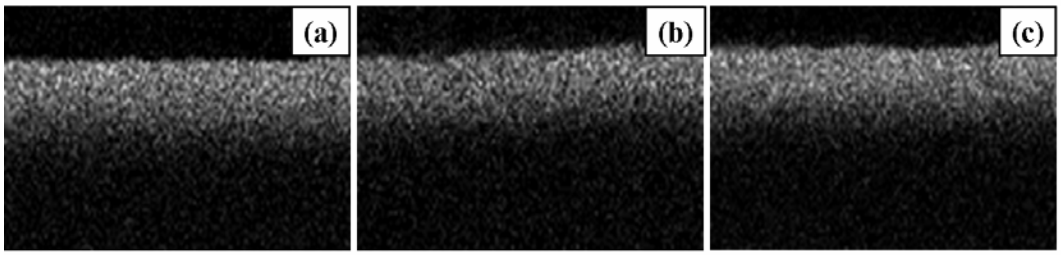

Fig. 8. The cross-section EDS mapping images of Pd of Pd-Cu-Ni ternary alloy membranes deposited on an porous nickel support and alumina modified porous nickel supports: the support are S700(a), A05S900(b), and A10S1000(c).

Table. 2. The surface weight composition of Pd-Cu-Ni ternary membrane deposited on porous nickel and alumina modified nickel support [%]

Membrane	Pd	Cu	Ni
Pd-Cu-Ni/S700	86.3	4.2	9.5
Pd-Cu-Ni/A05S900	87.2	4.3	8.5
Pd-Cu-Ni/A10S1000	88.7	4.2	7.1
Pd-Cu-Ni/S650[a][22]	89.0	4.5	6.5

a: Cu-reflow temperature was 650℃

were similar to each other as around 4㎛ which is similar to the previous study where the Cu-reflow temperature was 650 ℃. Fig. 8 shows that the Pd EDS mapping images to clarify the atomic interdiffusion of palladium into porous nickel. We can see that there were no indications of atomic interdiffusion of palladium into porous nickel at 700 ℃. From Table 2 and Fig. 8, we can insist that the weight compositions of Pd-Cu-Ni ternary alloyed membrane could be controlled by not only Cu-reflow temperature but also alumina coating amount. Further studies, what do the composition of ternary alloyed membrane effect on hydrogen permeation and membrane stability have to be carried out.

4. Conclusions

From SEM analysis, porosimeter and hydrogen permeation test it was found that a porous nickel support withstand up to 750. In order to increase the ℃ e thermal stability of porous nickel support, alumina was coated on the nickel powder by incipient wetness impregnation method and EDS analysis showed that alumina was well coated on nickel powder. From SEM and mercury porosimeter analysis, it can be insisted that not only alumina coating prohibit nickel sintering, melting down and pore plugging but also alumina coating amount increase the thermal stability up to 1000 ℃. Furthermore, ultra thin Pd-Cu-Ni ter-

nary alloyed membrane film of 4 ㎛ thickness was deposited by Pd and Cu sputtering followed by Cu-reflow at 700 ℃. And EDS mapping showed that Pd atomic interdiffuion was not carried out at that fabrication conditions. Moreover, EDS analysis shows that the weight composition of Pd-Cu-Ni ternary alloyed membrane could be controlled by not only Cu-reflow temperature but also alumina coating amount. Further studies, what do the composition of ternary alloyed membrane effect on hydrogen permeation and membrane stability have to be carried out. We hope that the alumina modified porous nickel support and Pd based composite membrane deposited on this kind of support could be applied into the high temperature demand processes such as methane steam reforming and solid-fuel gasification etc..

Acnologement

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