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Shaohua Chen[a]; Pifeng Xing[a]; Pengji Zhao[a]; Wenmei Chen[b]
[a] Institute of Nuclear Physics and Chemistry, Mianyang, P.R. China [b] School of Chemical Engineering, Sichuan University, Chengdu, P.R. China

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A PALLADIUM ALLOY COMPOSITE MEMBRANE FOR THE PURIFICATION OF HYDROGEN ISOTOPES

Shaohua Chen,[1,*] Pifeng Xing,[1] Pengji Zhao,[1] and Wenmei Chen[2]

[1]Institute of Nuclear Physics and Chemistry, CAEP, P. O. Box 919-214, Mianyang, 621900, P.R. China
[2]School of Chemical Engineering, Sichuan University, Chengdu 610065, P.R. China

ABSTRACT

In this study, experimental investigations were carried out on the deposition of Pd–Ag25at.% alloy on porous 316-type stainless steel substrate from ammoniacal solution by pulse electroplating, in order to prepare Pd–Ag alloy selective H-permeable membranes. The effects of the pulse electroplating conditions on the silver content, composition, morphology, and metallographical structure of the plated layers were studied. The film was evaluated by x-ray diffraction analysis. Besides the Pd–Ag alloy, there was a small amount of free silver ions in the layers that could be alloyed through annealing at 600°C. The silver content in the plated layers decreased with increase in the average current density and the conduction time. A high silver concentration in the plating solution was favorable for plating high silver content layers. Plated layers with silver content below 26 at.% had a bright

*Corresponding author. E-mail: csh19691216@163.com

appearance. The alloy phase featured with single and steady face centered cubic structure, and with the preferred orientation crystal face, being the lowest energy face (111). The results showed that the deposition rates of Pd–Ag alloy and silver were controlled by the mass transfer process of silver ammino complex. The Pd–Ag (25.7 ± 0.3)at.% alloy selective H-permeable membranes with 8 μm thickness were prepared using the pulse electroplating technology and the annealing method that developed in the experiments. At 300 and 350°C, the hydrogen permeability per unit area of this membrane was 27.6 and 28.5 mL(STP)/min cm^2, respectively, which was about 8.8 and 9.1 times higher than that of the commercial Pd–Ag25at.% alloy membranes, respectively, under the same condition with the operating pressure being 0.1 MPa. By using the prepared membrane, hydrogen of high purity could be obtained. After passing through this membrane, the He content in the gas mixture of 15%He–85%H_2(V/V) was reduced to as small as 0.03%. The results indicated that the clearing factor of this membrane was 375 for ^{3}He, and was higher than 500 for all the other impurity-gases. In summary, the prepared Pd–Ag alloy selective H-permeable membrane is potentially applicable for purifying the fusion fuel and for producing ultra-high pure hydrogen.

Key Words: Palladium alloy; H-Permselective membrane; Pulse electroplating; Crystal structure

INTRODUCTION

It is necessary to establish a fuel clean unit (FCU) and a hydrogen isotope separation system (HISS) for fission reactor to produce T (tritium) and for fusion–fission reactor to accomplish a fuel recycle. The FCU is mainly used in recovering D–T (deuterium–tritium) that comes from the reactor exhausted gases, in separating T that was produced in the reactor breeder blanket from elution gases, and in removing ^{3}He derived from the decaying of T because of its long-time storage (1,2).

Among all of the hydrogen isotope purification methods, the palladium alloy diffusion membrane separation is considered as one of the most promising methods because of its high hydrogen selective permeability, small inventory, simplicity, and continuable operation. Over the years, in order to test the feasibility of this method and to provide indispensable design and operation

parameters for the FCU, many investigators have studied a number of factors that probably affect hydrogen permeability of palladium alloy membranes (3–6). Furthermore, several tritium laboratories have successfully carried out the tritium demonstrative on-line experiments on palladium alloy membrane diffuser (7,8). However, currently employed commercial Pd–Ag23–25at.% alloy membranes are not satisfactory yet because of their low hydrogen permeability, poor mechanical strength, high operation temperature, and high cost. Therefore, it is still necessary to develop high-performance membranes with high H-permeability and high selectivity.

Previous investigations on this topic could be classified as follows. 1) Developing new palladium base alloy membranes, e.g., palladium–rare earth alloy membranes, palladium–copper alloy membranes, palladium–boron membranes, etc. Among these, Pd–Y (palladium–yttrium)7.5at.% alloy membrane has the maximum hydrogen permeation coefficient, which is two times higher than that of Pd–Ag23at.% membrane (9), but yttrium is a high-cost metal. 2) Developing selective H-permeable membranes operating at room temperature, e.g., polymer membranes (10) whose values of PR (permeation rate) are several orders of magnitude higher than that of the Pd–Ag membrane, but these membranes have poor hydrogen selectivity. 3) Developing supported Pd–Ag alloy selective H-permeable membranes. For this kind of membrane, its thickness is reduced from 80 μm, which is the thickness of commercial Pd–Ag alloy membranes, to several micrometers. As a result, the PR is increased considerably according to the Fick's law while the cost is reduced. By introducing the microporous substrate, the contradiction problem between the membrane thickness and the membrane mechanical strength could be solved (11). A number of literatures on this method reported that the PR values are several times higher or even up to one order of magnitude higher than that of the Pd–Ag membrane (12–15), but there was no detailed preparation technology reported in the patents. Furthermore, the Ag content was also less than 23at.%, which was the content in the Pd–Ag23at.% alloy that possessed the best hydrogen selective permeability and the best phase stable condition at the hydrogen isotope atmosphere.

In this study, using a porous 316-type stainless steel disc as the substrate, a Pd–Ag alloy membrane with thickness of several micrometers is prepared by pulse electroplating and multilayer electroplating. The composition of the prepared membrane is single and uniform, and the structure is stable and bonded tightly with the substrate. The relationships between the composition, the metallographic structure, and the annealing temperature are studied. The hydrogen selective permeation performance of this membrane and its feasibility employed in fusion fuel purification are also investigated.

EXPERIMENTAL

For the selective H-permeable membranes, Ag content should be controlled in the range from 23 to 25%. With such an Ag content, not only the stress resulting from the transformation of α phase palladium hydride to β phase palladium hydride can be overcome, but also the hydrogen permeation coefficient is higher than that with pure palladium (16). A number of investigations have been carried out on electroplating Pd–Ag alloy, but the content of Ag is generally more than 30% (12,17). The bright-plated layers of Pd–Ag23at.% can be prepared by using concentrated chloride solution, but the corrosivity of the plating solution is very serious to the substrate. By using the ammoniacal plating solution that has wide bright current density range, bright layers can be prepared. Many Pd–Ag alloy layers with different composition can be prepared by adjusting the current density (18,19), but the composition of the plating layer should be tested experimentally in order to check whether it is single and uniform or not. Recent studies showed that bright Pd–Ag23at.% or Pd–Ag25at.% membranes, with the same ratio of Pd to Ag in the plating solution, can be prepared by adding a little amount of glycocoll and glycinate in the ammoniacal plating solution (20). The substrates used in this study are porous discs, different from the solid materials used in the previous studies, and the electroplating technology is also different.

Preparation of Membrane

The two kinds of plating solution are as follows: (I) $Pd(NH_3)_4(NO_3)_2$, 0.067 *M*; $Ag(NH_3)_2(NO_3)$, 0.020 *M*; pH 11.8 ± 0.2; and (II) $Pd(NH_3)_4(NO_3)_2$, 0.067 *M*; $Ag(NH_3)_2(NO_3)$, 0.030 *M*; pH 11.8 ± 0.2.

For pulse electroplating, the average current density J_a is 10–30 mA/cm^2, the time ratio T_{on}/T_{off} of turning on to off is 1:4–1:9, the frequency is 1000 Hz, the current waveform is rectangular, and the temperature of plating solution is 23°C. The Ti electrode plated with Pt is used as anode and the microporous 316-type stainless steel disc with the maximum pore diameter of 3 μm is used as cathode. For direct electroplating, J is also 10–30 mA/cm^2, and the other parameters are the same as mentioned above.

After degreasing, the pores of the substrate are enclosed by zinc stearate. Then, the substrate is polished mechanically and degreased again. The substrate is actively pre-plated for 5 min with a 60 mA/cm^2 current density in a nickel chloride–chlorhydric acid (ratio 1:1) solution at room temperature. After pre-plating, the substrate is cleaned quickly with deionized water, and then is put into an electroplating bath without turning off the current and electroplated for 10 min. When the thickness of the plated layers reaches about 2 μm, the disc is taken out, cleaned, and dried.

Optical spectrometer (ICAP9000, Shenyang Scientific Instrument Development Center, Chinese Academy of Sciences) is used to determine the composition and the thickness of the layers. X-ray diffraction (XRD) spectrometer (Y-4Q, Shenyang Scientific Instrument Development Center, Chinese Academy of Sciences) is used to analyze the metallographic structure with Cu Kα target, graphite monochromator, wavelength being 1.54178 Å, and scanning rate being 0.02°/sec.

Annealing of Pd–Ag Alloy Membrane

The prepared Pd–Ag alloy membranes that supported on the substrate are annealed for 2 hr in an atmosphere of Ar gas, and the temperature is maintained in the range from 600 to 900°C during the process. The membranes are analyzed by XRD after being annealed at 600, 750, and 900°C, respectively.

Test of Hydrogen Permeation

The conspectus that is shown in Fig. 1 is used to test the hydrogen-selective permeable characteristics and the purification capability of the Pd–Ag alloy membranes. The feed gases are H_2 (99.999%) and mixture gases of 85%H_2–15%He, respectively.

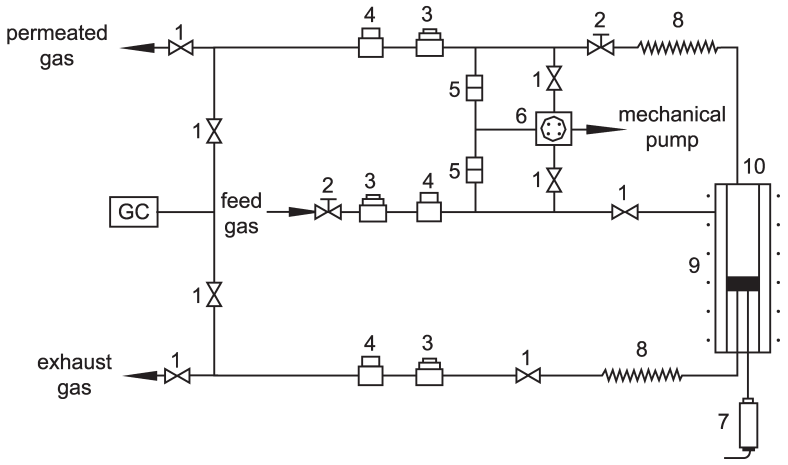

Figure 1. Conspectus of H-permeation experiment. (1) Closing valve; (2) constant-pressure valve; (3) electromagnetic steady flow valve; (4) mass flowmeter; (5) pressure sensor; (6) vacuum gauge; (7) thermal resistance; (8) condensator; (9) heater; (10) hydrogen permeating filter.

RESULTS AND DISCUSSIONS

Composition and Morphology

The silver content of the layers plated by pulse electroplating or direct electroplating decreases with increase in the average current density, as shown in Fig. 2. This indicates that high J_a (or J) strengthens the cathodic polarization,

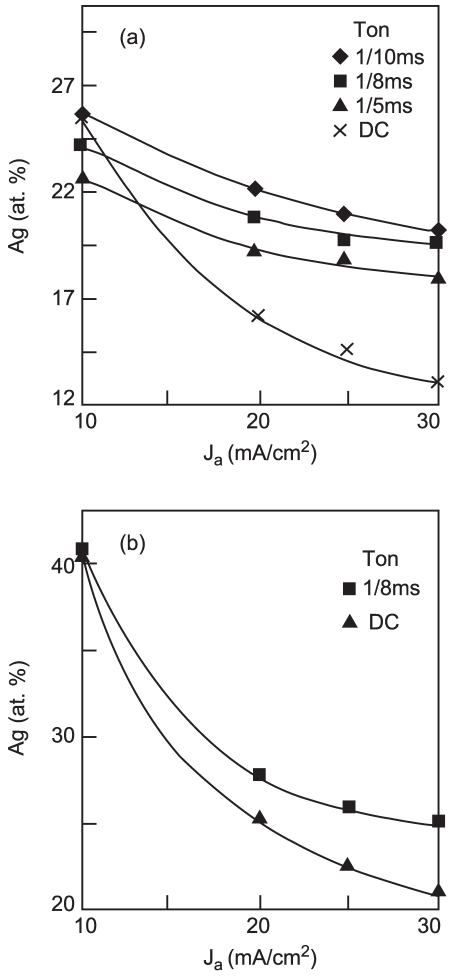

Figure 2. Relationship between the composition of the plated layers and the average current density. (a) Plating solution (I); (b) plating solution (II).

which prevents the silver ammino complex from transferring from the solution medium to the electropositive side of the electric double layer. Therefore, it may be concluded that the deposition rate of silver is controlled by the mass transfer process.

As shown in Fig. 2, the silver content of the layers increases with decrease in the conduction time at a certain value of J_a. Short conduction time T_{on} (or long cutting off time T_{off}) is favorable for the depolarization that accelerates the diffusion of silver ammino complex to cathodic surface. It is verified once again that the deposition rate of silver on the substrates is controlled by mass transfer process. At a certain current density, the silver content in the pulse electroplating layers is higher than that in the direct electroplating layers. Agitating the solution is favorable for the diffusion of silver, which then results in high silver content in the plated layers. This is consistent with the previous experimental results (19). The silver content in the plated layers is related to the silver concentration of the plating solution, and a high silver concentration of the solution is favorable for plating high silver content layers.

When J_a is 10 mA/cm^2 and T_{on} is 1/8 msec, the Pd–Ag41.2at.% layers that are obtained from plating solution (II) are black in appearance. When J_a is 20 mA/cm^2 and T_{on} is 1/8 msec, the Pd–Ag27.8at.% layers that are obtained from plating solution (II) are semi-bright in appearance. When J_a is 25 or 30 mA/cm^2 and T_{on} is 1/8 msec, the layers with silver content below 26% that are obtained from plating solution (II) and from plating solution (I) on all test conditions are all with bright appearance. Their apparent morphology micrograms are shown in Fig. 3.

Metallographical Structure

For the commercial Pd–Ag 25% alloy membrane with a thickness of 80 μm prepared by high-temperature smelting or mechanical cold-rolling, just like that of Pd or Ag is also an face centered cubic (f.c.c.) structure, and the

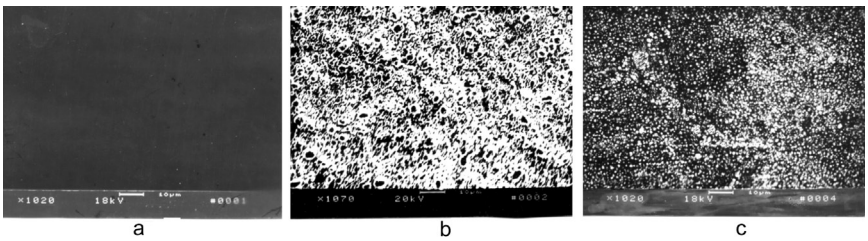

Figure 3. Microgram of the plated layers. (a) Brightness; (b) semi-brightness; (c) black.

preferred orientation is (200) face (as shown in Fig. 4). With different preparation technologies (20), face (220) is also possible to be the preferred orientation face.

It is known that the crystal cell parameters of Pd and Ag are 3.8830 and 4.0861 Å (21), respectively. According to these values and the Vegard equation, calculated crystal cell parameter of the commercial Pd–Ag25% alloy membranes is 3.934 Å, which is consistent with the value 3.935 Å measured by the XRD analyzer. However, the metallographical structure of the plated layers is not like that mentioned above, as shown in Fig. 5. In the XRD diagram of Pd–Ag alloy shown in Fig. 5, there is a weak diffraction peak near the $2\theta = 38.145°$. This indicates that a small amount of free silver lies in the Pd–Ag alloy membranes because the diffraction peak of silver crystal face (111) exists at $2\theta = 38.145°$.

The Pd–Ag alloy preferred orientation is the lowest energy crystal face (111), as shown in Fig. 6. Crystal cell parameters calculated from different crystal faces are different, e.g., $d_{111} \neq d_{200}$. When $J_a = 30\,\text{mA/cm}^2$, $T_{on} = 1/8\,\text{msec}$, and with the plating solution (II), the composition of the plated layers is Pd–Ag25.8% with XRD analyzed $d_{111} = 3.932$ Å and $d_{200} = 3.920$ Å. Under the same condition except for using plating solution (I), the composition becomes Pd–Ag18.9% with $d_{111} = 3.920$ Å and $d_{200} = 3.911$ Å. This indicates that the Pd–Ag alloy phase has a deformed f.c.c. structure, which will result in an inner stress in the plated layers. According to the width of the diffraction peak of the alloy phase (111) face and the Scherrer equation, the crystal size of the bright-plated layers is 130–340 Å, that of the semi-bright plated layers is about 380 Å, and that of the black-plated layers is 490 Å or so. Just as mentioned above, for the supported Pd–Ag alloy membrane prepared by the electroplating, both the composition and the high-temperature stability cannot meet the requirement of high hydrogen-selective permeability.

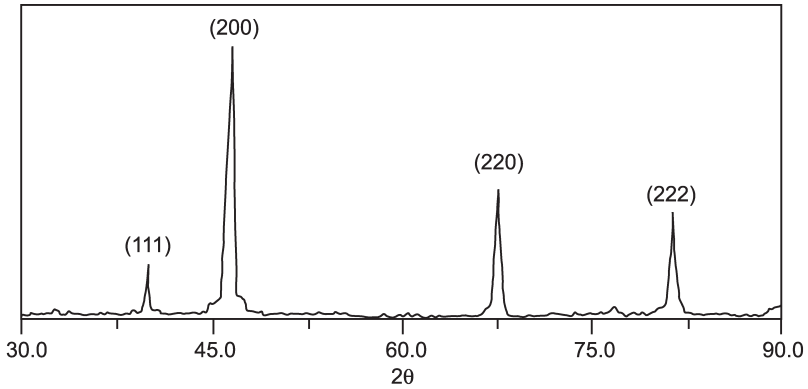

Figure 4. XRD diagram of the commercial Pd–Ag25% alloy membranes.

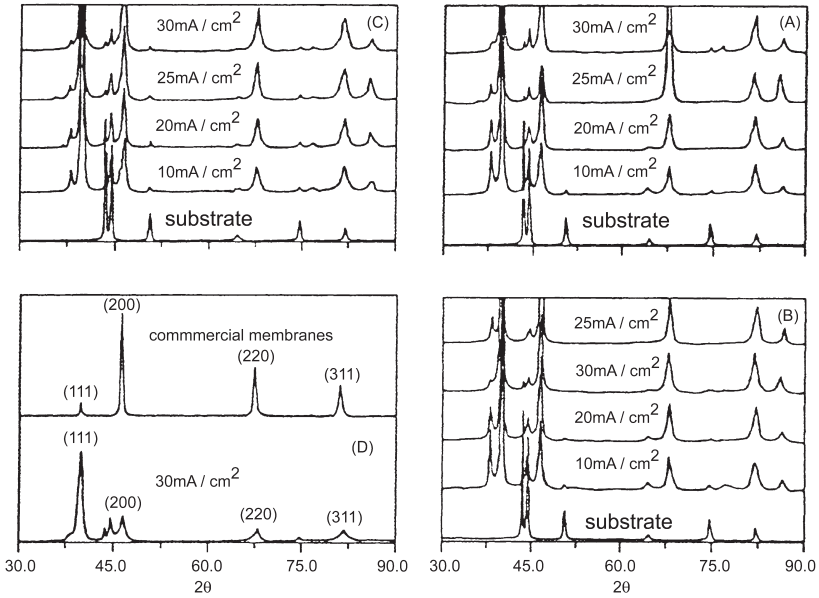

Figure 5. XRD diagram of Pd–Ag alloy plated layers (A, B, C). With plating solution (I); (D) with plating solution (II). (A) $T_{on} = 1/10$ msec; (C) $T_{on} = 1/5$ msec; (B, D) $T_{on} = 1/8$ msec.

To improve these indexes, it is verified that it is effective to anneal the membrane at a certain condition. The prepared membranes are annealed at 600°C for 2 hr, whose XRD peaks are narrower than that of the unannealed membranes, and the diffraction peaks of pure silver are not detected in the range $2\theta = 35–75°$, as shown in Fig. 6. This indicates that the Pd–Ag alloy crystal has grown through annealing, and all of the free silver has been alloyed. The measured crystal cell parameters are $d_{111} = d_{200} = d_{220} = 3.931$ Å, which verifies that the annealing enables the plated layers transform from an unsteady deforming lattice to a steady f.c.c. structure. At the same time, the inner stress in the plated layers is eliminated. According to the Vegard equation, the calculated composition of the annealed supported Pd–Ag alloy membrane is Pd–Ag24.3at.%. The silver content is obviously lower than that of the unannealed; maybe it is due to that the silver volatilizes to the gas phase and diffuses to the substrate at high temperatures.

After annealing at 900°C, the composition of the prepared membranes almost completely changes from Pd–Ag alloy and free silver phases to silver-rich Ag–Pd alloy and palladium-rich Pd–Ni alloy phases, as shown in Fig. 6, in which the nickel comes from the pre-plating layers and the substrate. The crystal

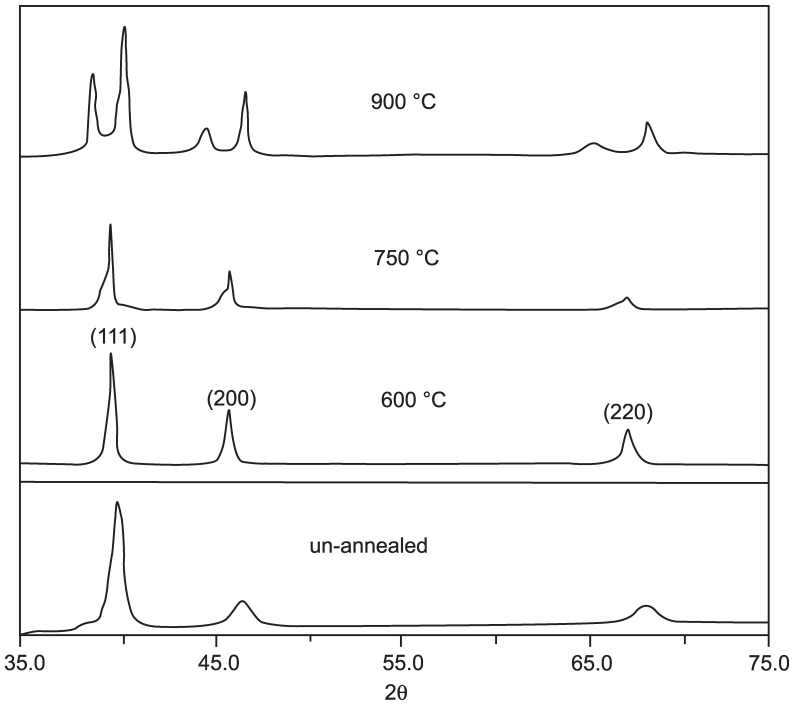

Figure 6. XRD diagram of the supported Pd–Ag alloy membranes (annealing for 2 hr).

cell parameters of the Ag–Pd alloy phase are $d_{111} = d_{200} = 4.023$ Å, and that of the Pd–Ni alloy phase are $d_{111} = d_{200} = 3.854$ Å. The compositions of these two are Ag–Pd7at.% and Pd–Ni8at.%, respectively. In fact, at 750°C, a part of the Pd–Ag alloy has been changed into Ag–Pd alloy and Pd–Ni alloy. In brief, when this membrane is annealed at 600°C for 2 hr under a high pure argon atmosphere, the composition and structure parameters are similar to that of the commercial Pd–Ag selective H-permeable membranes, and the interdiffusion between the nickel in the substrate and the silver in the membranes ensures enough binding force between them.

Deposition Mechanism

Generally, the electrodeposition of Pd–Ag alloy undergoes the following main processes. 1) Mass transfer of silver ammino complex or palladium ammino complex from the bulk solution to the electropositive side

of the electric double layer of the cathode; 2) electric-charge transfer of the absorption atoms formed by the complex crossing the electric double layer on the electrode; 3) diffusion of the absorbed atoms onto the electrode surface to form nucleus; and 4) crystal growth.

The silver deposition rate is controlled by the mass transfer process parameters, including the relationships between the total silver content of the plated layers and the average current density, the conduction time, and the agitating rate. Not all silver is alloyed; maybe its dissolving process in the palladium is the key step for the alloy phase depositing rate. According to this, the lattice parameter or silver content of the alloy phase should decrease with the increase in the average current density just like the free silver because silver could be infinitely dissolved in palladium. However, it is obviously not consistent with the experimental results shown in Fig. 7. Therefore, the deposition rate of alloy phase is also perhaps controlled by the diffusion process of the silver in the solution.

In fact, the formation of silver crystal nucleon and that of Pd–Ag alloy crystal nucleon are two parallel competitive reactions. Silver content in the Pd–Ag alloy crystal nucleon and the numbers of crystal nucleon are related to the energy provided from outside. It is easy to form alloy crystal nucleon with low silver content under the low current density, and vice versa. When current density rises up to a certain level, it tends to form higher silver content in the alloy crystal nucleon; however, as there are not enough silver atoms, only a low silver content alloy crystal nucleon and related Pd–Ag alloy are formed as a result. The result in Fig. 7 is exactly the macro-reflection of such a process.

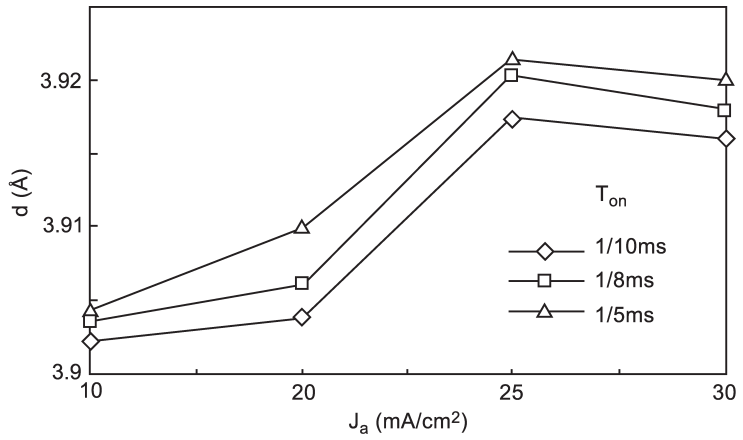

Figure 7. Relationship between the lattice parameter of the alloy phase (111) face and the current density.

Hydrogen Permeability of the Membranes

Pd–Ag(25.7 ± 0.3)at.% alloy membranes with 8 μm thickness are prepared under conditions described as follows: average current density is 30 mA/cm^2, the time ratio T_{on}/T_{off} of turning on to off is 1:7, conduction time is 1/8 msec, plating solution is 0.067 M $Pd(NH_3)_4(NO_3)_2$ and 0.030 M $Ag(NH_3)NO_3$, pH = 11.8 ± 0.2, and T = 23°C. These parameters are selected according to the experimental results that are discussed above.

Gas penetrability of the 316-type stainless steel filter with 3 μm maximum pore diameter is detected before and after pre-plating. The gas penetrating rate for ^{3}He is 1833 mL(STP)/min cm^2 at an operating pressure of 0.1 MPa before pre-plating, and that drops to 720 mL(STP)/min cm^2 after pre-plating. Pre-plating could result in the decrease of the pore diameter, but it does not affect the hydrogen permeability at such a high gas-penetrating rate. In order to test whether the gas will leak from the supported Pd–Ag alloy membranes or not, experiments are carried out by feeding 0.1 MPa ^{3}He into the upper part of the permeating system at 400°C, after vacuumizing the lower part. The driving pressure is 0.9 MPa and the back pressure is 0.1 MPa. After maintaining this condition for 6 hr, the operating pressures do not change at all. This indicates that there is no leakage from the membrane.

The hydrogen selectivity and permeability of this supported membrane is tested using the conspectus that is shown in Fig. 1. The driving pressure is 0.2 MPa, and the backpressure is 0.1 MPa. At 300 and 350°C, the hydrogen PRs are 458.5 and 473.4 mL(STP)/min, respectively. The effective area of this supported Pd–Ag alloy membrane that is in contact with hydrogen is 16.6 cm^2 (Φ46 mm); accordingly the PR values are 27.6 and 28.5 mL(STP)/min cm^2, respectively. At the same operating pressure with temperature being 350°C, the measured PR value of the mechanically rolled commercial Pd–Ag25at.% membrane with 80 μm thickness is 3.2 ml(STP)/min cm^2, which is consistent with the value in reference (22). Therefore, the PR value of the mechanically rolled commercial Pd–Ag25at.% membrane is about 9.1 times less than that of the prepared supported Pd–Ag alloy membranes. To deal with the gases containing tritium, it is better to use thinner supported Pd–Ag alloy membranes rather than using thicker commercial Pd–Ag alloy membranes, according to the consideration of either reducing the cost or reducing the volume of the hydrogen permeation to decrease the leakage of tritium to environment.

The H-permeable selectivity of the prepared supported Pd–Ag alloy membrane is tested at 300°C by using H_2(85%)–He(15%) mixture gases. After purification by this membrane, the He content contained in the hydrogen is only 0.03%. This result is not satisfactory enough for the preparation of ultra-pure hydrogen, for which the reason may be that the hydrogen permeation assembly, vacuum valves, and the sealing ferrules used in this work are all low-vacuum

devices. Anyway, for the purification of fusion fuel, the purification capability of this supported Pd–Ag alloy membrane is large enough.

FEASIBILITY AND APPLICABILITY

Purification capability of the supported Pd–Ag alloy membranes for hydrogen isotopes is related to the components and quantity of the impurities contained in the hydrogen gases. The D–T specific burn-up of each fuel cycle in the fusion–fission reactor is only 5–15%, i.e., the upper limit of the total impurity quantity in the exhaust gases that discharged from the plasma cell is about 15%, which is approximately equal to the quantity of ^{3}He that formed by the decay of the tritium during the storage period of 3 years. The permeating mechanism of hydrogen isotopes through the Pd–Ag alloy membrane is atom diffusion, but for other gases it is molecular diffusion. For the molecular diffusion, the diffusion coefficient is inversely proportional to the mass of the corresponding gaseous molecules. The clearing factors of the supported Pd–Ag alloy membranes for other impurities gases excepting ^{3}He are all higher than 500, and for ^{3}He, it is 375. Because the main component in the actual sample is not H_2 but DT or T_2, the isotope effect must be considered when purification capability of the supported Pd–Ag alloy membranes is estimated. The permeability coefficient ratio of H, D, and T permeating through the Pd–Ag25% alloy membranes is 1:0.65:0.58 (3,23). After getting purified by the supported Pd–Ag alloy membrane, the total quantity of impurities in the exhaust gases that discharged from the reactor will be less than 0.05%, and the content of ^{3}He contained in the tritium that has been stored for 3 years will be decreased down to 0.07%. After purification, the impurity quantity in the D–T mixtures is required to be less than 1% by HISS. As far as the purification capability is concerned, the supported Pd–Ag alloy membranes are considered capable of meeting the requirement of the fusion fuel purification. One piece of these membranes with an effective area of 16.6 cm^2 could deal with 58.7 g hydrogen per day (24 hr per day). While considering the isotope effect, it could deal with about 76 g deuterium or 102 g tritium per day. Therefore, as far as hydrogen permeability is concerned, the supported Pd–Ag alloy membranes are also capable of meeting the requirement of fusion fuel-processing.

CONCLUSIONS

The effects of pulse electroplating conditions on the silver content, composition, apparent morphology, and metallographical structure of the plated layers are studied during Pd–Ag alloy deposition on porous 316-type stainless

steel from ammoniacal solution by pulse electroplating. The plated layers are composed of Pd–Ag alloy and free silver that can be alloyed through annealing. Alloy phase is featured with an f.c.c. structure, and the preferred orientation crystal face is the lowest energy (111) face. The silver content of the plated layers decreases with increase in the average current density and the conduction time. A high silver concentration in the plating solution is favorable for depositing high silver content layers. Plated layers with silver content below 26 at.% have bright appearance. The results in this study show that the deposition rates of Pd–Ag alloy and silver are controlled by the mass transfer process of the silver ammino complex. The Pd–Ag(25.7 $\pm$ 0.3)at.% alloy membranes with 8 μm thickness supported on porous 316-type stainless steel substrates are prepared using the pulse electroplating and annealing technologies developed in the experiments. At 350°C, hydrogen PR of these membranes is 9.1 times higher than that of the commercial Pd–Ag25at.% alloy membranes under the same operating conditions. When H_2(85%)–He(15%) mixture gases are purified by the prepared membrane, the He content remaining in pure hydrogen is as low as 0.03%. The results indicate that the clearing factor of this membrane for ^{3}He is 375, and those for other impurity gases are all higher than 500. This work shows that the prepared supported Pd–Ag alloy selective H-permeable membranes are potentially applicable for purifying fusion fuel and for producing ultra-pure hydrogen.

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