

Application of Palladium Coating on Group 5 Metals for Vacuum Permeator —Possible Problems and Solutions—

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Permeation of hydrogen through Pd-Ta-Pd composite membrane was measured at 500 and 600 °C to examine the feasibility of the concept to use this type of membrane as permeation window to recover tritium from liquid Pb-Li alloy. At 500 °C, the permeation rate gradually decreased with increasing operation time due to surface contamination by carbon. These observations indicated that partial pressures of residual hydrocarbons in vacuum permeator have to be strictly controlled to avoid carbon deposition. Nevertheless, permeability could be restored by removal of carbon through reaction with O₂ gas. At 600 °C, however, permanent degradation took place due to development of open porosity in Pd layer and interdiffusion between Pd and Ta. Preparation of HfN intermediate layer between Pd and Ta hindered the porosity development and interdiffusion.

Keywords: Tritium Recovery, Permeation, Tantalum, Palladium, Fusion Blanket

I. INTRODUCTION

Tritium recovery by vacuum permeation is proposed in dual coolant Pb-Li breeder blanket concept [1]. Group 5 metals (V, Nb and Ta) are potential candidates of tube material because of high permeability of hydrogen isotopes and sufficient compatibility with liquid Pb-Li alloy. It, however, is known that the permeability of hydrogen isotopes is sensitively influenced by surface impurities. Terai et al. [2] have examined the feasibility of an Nb permeation window and reported that permeation rate of deuterium was much smaller than that expected from diffusivity and solubility of deuterium in Nb due to the growth of oxide films on surfaces. Hatano et al. [3-5] have reported that severe permeability deterioration is possible even in ultrahigh vacuum without oxide growth at elevated temperatures due to the formation of oxygen

adlayer through surface segregation from the bulk. Preparation of Pd coating is common way to solve this type of problems.

One of the biggest problems for such Pd-group 5 metal composite membrane is stability of Pd layers at elevated temperatures. In dual coolant Pb-Li breeder blanket concept, the expected operation temperature of vacuum permeator is 700 °C [1]. It has been reported that Pd layers prepared on V [6], Nb [7-9] and Ta [10] react with substrate metals at/below this temperature. In the previous study, the present authors found that high temperature stability of Pd on Ta is superior to that of Nb [11], but details have not been examined. From these viewpoints, hydrogen permeation through Pd-Ta-Pd composite membrane was examined at elevated temperatures in the present study.

II. EXPERIMENTAL

II.A. Permeation Experiment

Both sides of disk-type Ta specimens (20 mm diameter and 0.5 mm thickness) were polished with abrasive papers, and finished with diamond powder (9 and 3 μm) and colloidal silica (0.04 μm). Thin Pd layers (270 nm thickness) were prepared on both sides by magnetron sputtering at 300 °C. The specimen surface was cleaned by rf-sputtering in the sputtering apparatus prior to the preparation of Pd layers.

Permeation rate of hydrogen through the specimen was measured at 500 and 600 °C with a vacuum device evacuated to 10^{-6} Pa by a turbomolecular pump and an oil-sealed rotary pump. The device was separated into two chambers, i.e. up- and downstream chambers, by the specimen sealed with metal gaskets (U-Tightseal, Usui Kokusai Sangyo Kaisha, Japan). The pressure of hydrogen in the upstream chamber was kept at 1.0 Torr (0.13 kPa), and that of hydrogen permeating through the specimen into the downstream chamber was measured by a calibrated quadrupole mass analyzer and capacitance manometer. The pressure in the downstream chamber was maintained to be sufficiently low in comparison with the upstream by continuous pumping at known pumping speed. The permeation flux was calculated with the pumping speed and pressure.

II.B Surface Characterization

The change in reaction rate of hydrogen on the specimen surface with heat treatments was examined by absorption experiments at 300 °C. Sheet-type Ta specimens with Pd layer (270 nm) on one side was prepared from the same plate as the specimens for permeation experiments, and installed in a quartz tube attached to a different vacuum apparatus evacuated to 10^{-6} Pa by a turbomolecular pump and an oil-sealed rotary pump. After heat treatment in vacuum at 300 °C

for 1 h, the specimen was exposed to air at room temperature for 1 h. Then hydrogen absorption rate was examined at 300 °C. The initial pressure of H_2 gas was adjusted to be 13 Pa. Oxide film was recovered on the area where Ta was appearing on the surface, and the absorption took place only through Pd layer under the present conditions. The exposure to air at room temperature and the absorption measurements at 300 °C were repeated after each heat treatment in vacuum at 400, 500, 600 and 700 °C for 1 h. The detailed procedure is described in Refs. [8] and [9].

The specimen surfaces before and after the heat treatments in vacuum were analyzed with Auger electron spectroscopy (AES), scanning electron microscopy (SEM) combined with energy dispersive X-ray spectroscopy (EDS) and X-ray diffractometry (XRD), and those after the permeation experiments were examined by SEM-EDS.

III. RESULTS AND DISCUSSION

Fig. 1 (a) shows SEM image of the specimen under the as-prepared conditions. It is shown that polycrystalline Pd layer was formed on Ta and grain size was about 300 nm. Palladium was a sole element detected by EDS as shown in Fig. 1 (b). The X-ray diffraction pattern under the as-prepared conditions is shown in Fig. 2. Peaks of Pd and Ta were observed, and there was no visible peak of impurity or second phase.

The change in permeation rate at 500 °C with time is plotted in Fig. 3. Initial value of permeation rate was 5×10^{-8} mol H_2 $\text{m}^{-1}\text{s}^{-1}\text{Pa}^{-1/2}$. This value is smaller than the permeation rate evaluated from the equation proposed by Lässer [11] from data on hydrogen diffusivity and solubility in Ta (1.3×10^{-7} mol H_2 $\text{m}^{-1}\text{s}^{-1}\text{Pa}^{-1/2}$), but the difference is small. The permeation rate gradually decreased with time, and it reached a half of initial value after operation for 30 h.

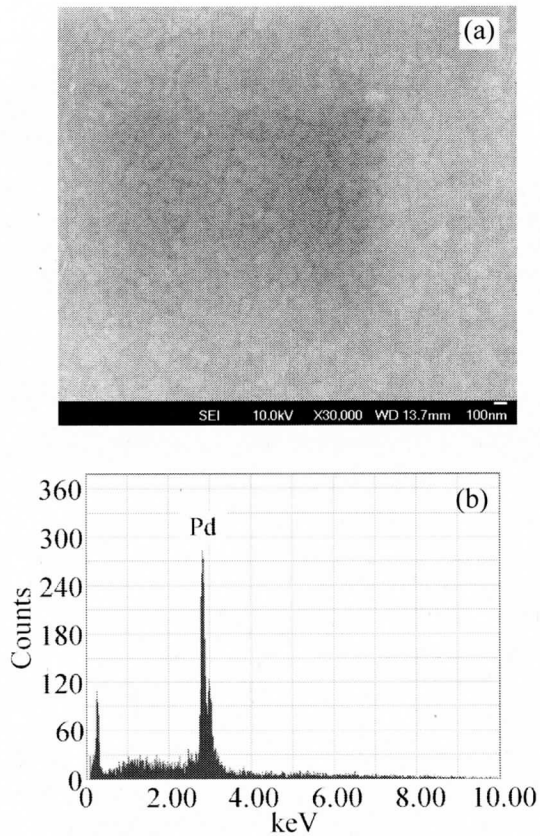


Fig. 1 (a)SEM image and (b)EDS spectrum of Pd/Ta specimen as-prepared.

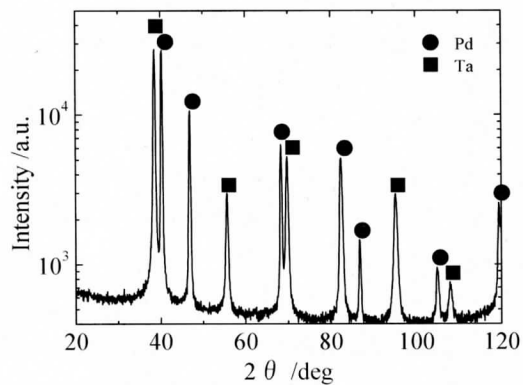


Fig. 2 XRD diffraction pattern of Pd/Ta specimen as-prepared.

In the absorption experiments, significant reduction in surface reaction rate was observed after heating the specimen at 600 °C for 5 h. The analysis by AES showed that the surface of Pd layer was severely contaminated by carbon as shown in Fig. 4. The surface reaction rate was recovered for certain extent after gentle

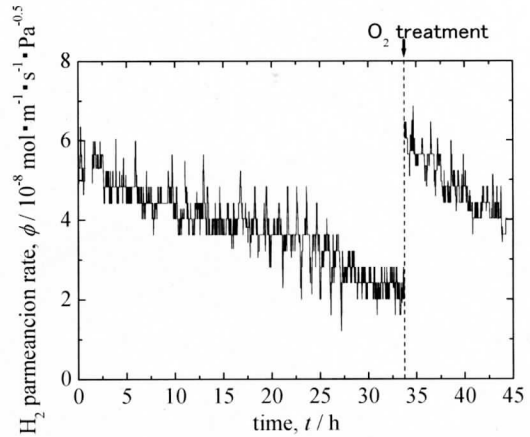


Fig. 3 Change in permeability of H₂ for Pd/Ta/Pd at 500 °C.

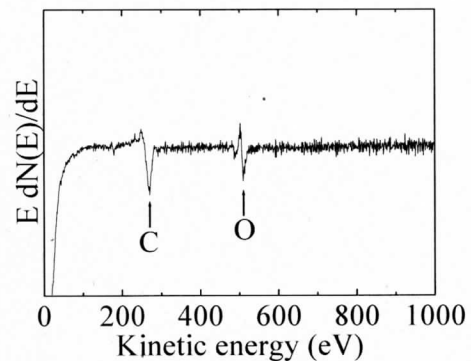


Fig. 4 AES spectrum for Pd/Ta after heating at 600 °C for 5 h.

sputtering to remove carbon.

In order to understand the effect of carbon in the permeation experiments, O₂ gas was introduced in both of up- and downstream chambers to 13 Pa, and the specimen was heated at 400 °C for 1 h. As shown in Fig. 3, the permeability was restored completely by this treatment in O₂ gas. Hence, it was concluded that the reduction in permeability shown in Fig. 3 was due to contamination by carbon, and removal of carbon as CO or CO₂ led to restoration of permeability. The source of carbon is considered to be hydrocarbons present in the devices as residual gases. These observations indicate that partial pressures of residual hydrocarbons in vacuum permeator have to be strictly controlled to avoid deterioration in permeability. This type of degradation, however,

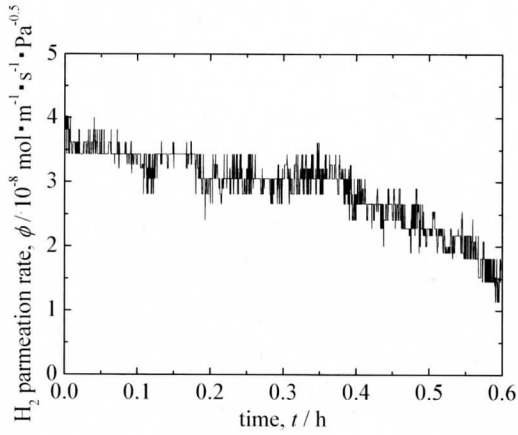


Fig. 5 Change in permeability of H₂ for Pd/Ta at 600°C.

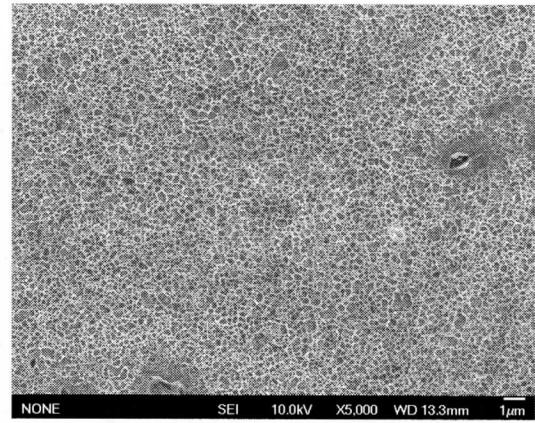


Fig. 7 SEM image of Pd/Ta after heating at 700°C for 1 h.

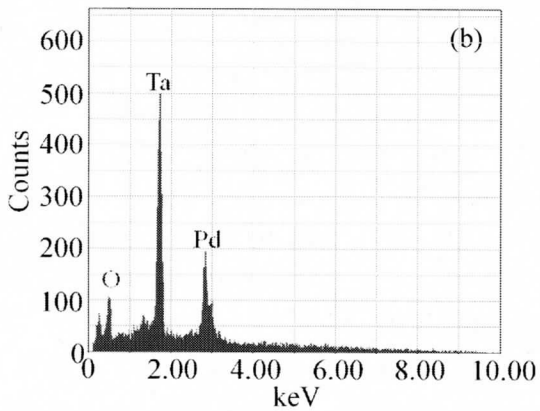
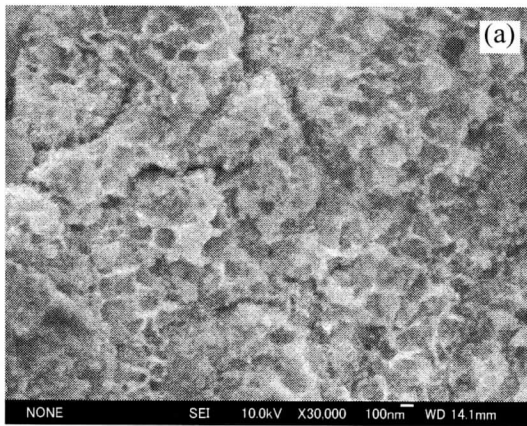


Fig. 6 (a) SEM image and (b) EDS spectrum of downstream side for Pd/Ta/Pd after hydrogen permeation at 600 °C.

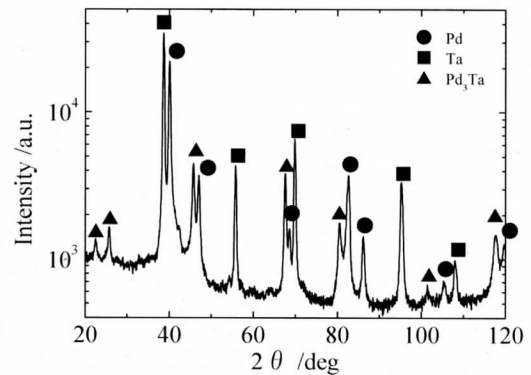


Fig. 8 XRD diffraction pattern of Pd/Ta after heating at 700°C for 1 h.

is *reversible* and the permeability can be restored by heat treatment in O₂ gas.

Fig. 5 shows the change in permeability with time at 600 °C. Initial value of permeation rate was $4 \times 10^{-8} \text{ mol H}_2 \text{ m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1/2}$, and this

value is slightly smaller than the permeation rate evaluated from the equation proposed by Lässer [12] ($9.3 \times 10^{-8} \text{ mol H}_2 \text{ m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1/2}$). The reduction in permeation rate was observed also at 600 °C as shown in this figure. In order to examine whether restoration of permeability is possible at this temperature, air was introduced to up- and downstream chambers to 10^{-2} Pa with keeping specimen temperature at 600 °C. This treatment, however, resulted in *irreversible* change in surface state. Namely, the color of surface changed from shiny metallic gray to black. Fig. 6 (a) shows SEM image of downstream side surface after this treatment as an example. This figure indicates increase in surface roughness. In the X-ray spectrum, large peak of Ta was observed together with that of O in addition to Pd as shown in Fig. 6 (b). These observations

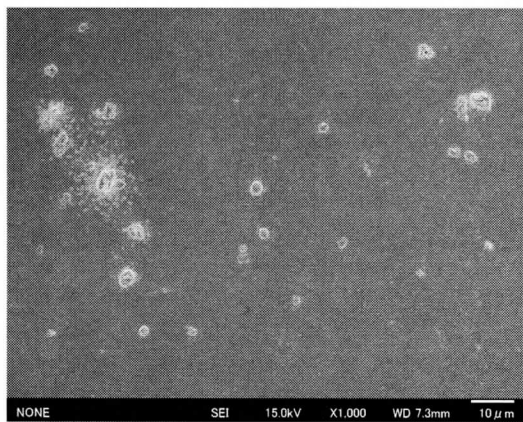


Fig.9 SEM image of Pd/HfN/Ta after heating at 700°C for 1 h.

suggest that Ta oxides were formed on the specimen surface.

In order to understand the mechanism underlying Ta oxides formation, the specimen heated in vacuum at 700 °C for 1 h was examined by SEM-EDX and XRD. As shown in Fig. 7, porous structure was developed by the heat treatments. Formation of intermetallic compound (Pd_3Ta) was also indicated by XRD analysis (Fig. 8). These observations suggest that Ta appeared on the surface during permeation experiment at 600 °C due to open porosity development and interdiffusion, and reacted with oxygen during the above-mentioned treatment in 10^{-2} Pa air. It was therefore concluded that Pd layer in several hundreds nm thickness cannot keep its coating effects at operation temperature of vacuum permeator.

One of the ideas to solve this type of problems is to increase the thickness of Pd layer drastically, but it should be accompanied by significant increase in the cost and difficulties in fabrication. Reduction in operation temperature led to poor thermal efficiency of the reactor. From these viewpoints, the intermediate layer to prevent the reaction between Pd and Ta has been developed by the present authors. Fig. 9 shows the SEM image of the specimen with Pd layer (270 nm) prepared on HfN intermediate after heating at 700 °C for 1 h. The HfN layer was

prepared arc-plasma gun (ULVAC Co., Japan) under 0.3 Pa N_2 gas atmosphere, and its thickness was 70 nm. Blisters (2 – 20 μm diameter) were found on the surface after the heat treatment at 700 °C as shown in this figure. Nevertheless, development of open porosity was not observed. In addition, intermetallic compound was not detected in XRD analysis. The permeation experiments with the specimens having HfN intermediate layer is currently in preparation, and results will be reported in future.

IV. SUMMARY

The permeation of hydrogen through Pd-Ta-Pd composite membrane was examined at elevated temperatures to understand the applicability of this type of composite membrane to tritium recovery from liquid Pb-Li alloy. The composite membrane was degraded during operation by two different mechanisms: *reversible* degradation by carbon deposition, and *irreversible* degradation by interdiffusion and open porosity development. In the former case, the permeation rate could be restored by removal of carbon through the reaction with oxygen. In the case of latter, however, degradation was permanent. It was shown that the preparation of thin HfN intermediate layer hinders open porosity development and interdiffusion.

Acknowledgments

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