

# Improvement of high temperature stability of Pd coating on Nb by intermediate layer comprising NbC and Nb<sub>2</sub>C

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Received 24 September 2006; received in revised form 19 January 2007; accepted 19 January 2007

Available online 24 January 2007

## Abstract

Non-porous intermediate layers comprising NbC and Nb<sub>2</sub>C were prepared between thin Pd films (100 nm) and Nb substrates, and the high temperature stability (573–873 K) of Pd coating was examined by hydrogen absorption experiments. This type of intermediate layer provided better stability of Pd coating at/below 673 K than the layers consisting solely of Nb<sub>2</sub>C. Sharp reduction and recovery in hydrogen absorption rate were observed after heat treatments at 773 and 873 K, respectively. The mechanism underlying such complicated temperature dependence was discussed.

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*Keywords:* Hydrogen absorbing materials; Composite materials; Surfaces and interfaces; Solid state reaction; Diffusion

## 1. Introduction

Hydrogen separation membranes are key components of membrane reactors for hydrogen production via, for example, steam reforming of natural gas [1]. Group 5 metals (V, Nb and Ta) have higher hydrogen permeabilities, lower prices and richer natural resources than Pd which has been widely used as a membrane material. Surfaces of group 5 metals, however, are sensitive to poisoning by impurities such as oxygen, and hence it is common to prepare thin Pd films on the surfaces of permeation membranes as protection layers [2–12]. The hydrogen permeability of such composite membranes, however, declines at elevated temperatures (>673 K) due to the degradation in coating effect caused by interdiffusion between Pd and base metals [6,7].

Edlund et al. [6,7] developed porous oxide intermediate layers to prevent the interdiffusion between Pd and V. The Pd layers employed in their study, however, were rather thick (25 μm), and hence the amount of Pd necessary to prepare the composite membrane was comparable with conventional Pd membranes. The present authors have prepared non-porous Nb<sub>2</sub>C intermediate layers between thin Pd films (100 nm) and

Nb substrates and examined the high temperature stability of the Pd films at temperatures from 573 to 773 K [13]. They found that the coating effect of Pd films prepared without the intermediate layer was degraded rapidly by heating due to the development of open porosity. The preparation of the Nb<sub>2</sub>C intermediate layers resulted in significant improvement in the high temperature stability of Pd coating without deterioration in hydrogen permeability; the extent of open porosity development was strongly reduced by the Nb<sub>2</sub>C intermediate layer. The degradation in the coating effect, however, could not be suppressed completely.

In the present study, the intermediate layer consisting of NbC and Nb<sub>2</sub>C was prepared by increasing the extent of carburization of Nb substrates. The effect of this type of intermediate layer on high temperature stability of Pd coating was examined by measuring hydrogen absorption rate after heat treatments at temperatures from 573 to 873 K and compared with the influence of the intermediate layers comprising solely Nb<sub>2</sub>C.

## 2. Experimental

Disk-type specimens (10 mm in diameter and 0.5 mm in thickness) were prepared from a rod of pure Nb supplied by Nilaco (99.9 mass% purity). Their surfaces were polished with abrasive papers and finished with Al<sub>2</sub>O<sub>3</sub> powder of 0.06 μm. These specimens were carburized by heating at 1173 K for 30 min (1.8 ks) in a mixture gas of CH<sub>4</sub> (10%) and H<sub>2</sub> (90%) at atmospheric pressure, and then heated in vacuum at 1373 K for 5 h (18 ks) to saturate the bulk by carbon. The layers of Nb<sub>2</sub>C whose thickness was about 300 nm were formed by

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these treatments [13]. Some of these specimens was additionally carburized at 1173 K for 10 min (600 s) to form NbC and then heated in vacuum at 1373 K for 1 h (3.6 ks). The analyses by means of X-ray diffraction (XRD) showed that NbC was formed in addition to Nb<sub>2</sub>C by this treatment.

Thin Pd films whose thickness was 100 nm were prepared on both surfaces of specimens by vacuum deposition in a separate apparatus. After installation, the specimens were heated in vacuum ( $10^{-6}$  Pa) at 1000 K for 4 h (14.4 ks) to remove oxide films formed on the surfaces during the transportation of specimens in air; dissolution of oxygen into the bulk by heating led to the removal of oxide films. Then Pd was deposited onto the surfaces at room temperature up to 100 nm at a rate of 0.05 nm/s. The specimens with the Nb<sub>2</sub>C intermediate layer are hereafter denoted as Specimen A, and those with the intermediate layer comprising NbC and Nb<sub>2</sub>C as Specimen B.

The stability of Pd coating was examined in a temperature range from 573 to 873 K using a vacuum apparatus which was similar one used in the previous study [14]. First, the specimen was heated in vacuum ( $10^{-4}$  Pa) at 573 K for 1 h (3.6 ks). After being cooled down to room temperature, the specimen was exposed to air for 1 h (3.6 ks). Then, the durability of Pd coating was examined by measuring hydrogen absorption rate at 573 K in a closed vacuum system, in which the hydrogen absorption was indicated by pressure drop. This procedure including heat treatment, exposure to air at room temperature and hydrogen absorption experiment at 573 K was repeated at higher heat treatment temperatures; the specimen was subjected to a series of heat treatments at 623, 648, 673, 773 and 873 K, and each heat treatment was followed by the exposure to air and the hydrogen absorption experiment. Niobium oxides should be formed by the exposure to air at room temperature if open porosity is developed in Pd films during prior heat treatment, and consequently the hydrogen absorption rate at 573 K should be reduced [13]. The initial pressure of H<sub>2</sub> gas in hydrogen absorption experiment was adjusted to be 13.3 Pa. This value of H<sub>2</sub> pressure is significantly smaller than the upstream H<sub>2</sub> pressures commonly employed in the permeation experiments in this field [3–12]. In general, however, the rates of hydrogen absorption and permeation become more sensitive to surface states as pressure decreases [15]. Hence, the experiments in the low H<sub>2</sub> pressure appeared to be suitable to examine the stability of coating effects. Before and after hydrogen absorption experiments, the specimens were analyzed by means of XRD and scanning electron microscopy (SEM) combined with energy-dispersive X-ray analysis (EDX).

### 3. Results and discussion

Fig. 1(a) shows typical hydrogen absorption curves observed at 573 K for Specimen A. In the case of this specimen in as-prepared conditions (i.e. no heat treatment), the pressure of hydrogen dropped rapidly due to the absorption by the specimen. The rate of hydrogen absorption, however, decreased with increasing temperature of heat treatment. As described in the previous paper [13], such decline in hydrogen absorption rate was ascribed to the development of open porosity in the Pd coating caused by interdiffusion between Pd and Nb. The development of open porosity should result in the appearance of Nb on the surfaces and formation of Nb oxides by the exposure to air carried out after the heat treatments. Since Nb oxides strongly impede hydrogen absorption at 573 K, regions on specimen surfaces covered by Nb oxides should not contribute to hydrogen absorption [13]. Consequently, the rate of hydrogen absorption decreases with the progress of porosity development. The extent of reduction in hydrogen absorption rate shown in this figure was significantly smaller than that for the specimen without the intermediate layer as previously reported [13].

Typical results for Specimen B are shown in Fig. 1(b). The hydrogen absorption rate in the as-prepared conditions was slightly smaller than that of Specimen A. Reduction in the hydro-

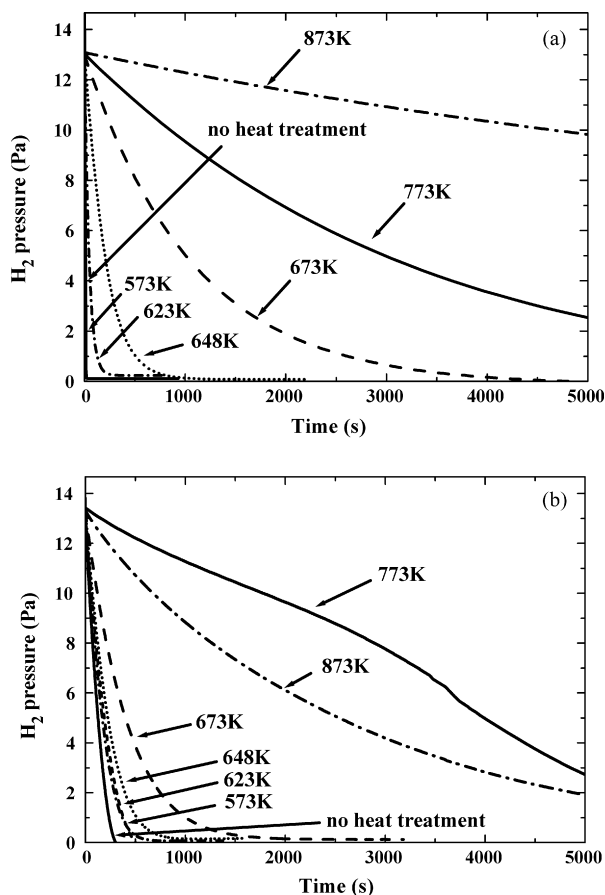


Fig. 1. Typical hydrogen absorption curves obtained for: (a) Specimen A and (b) Specimen B at 573 K. The temperatures indicated in the figures are those of heat treatments in vacuum.

gen absorption rate began to appear after the heat treatment at 673 K. The extent of reduction, however, was clearly smaller than that of Specimen A; i.e. the hydrogen absorption rate after the heat treatment at 673 K was higher for Specimen B than for A. This observation indicates that the stability of Pd coating was improved by the presence of NbC in this temperature range. Sharp reduction in hydrogen absorption rate was unexpectedly observed after the heat treatment at 773 K. It was, however, followed by the recovery in hydrogen absorption rate by the heat treatment at 873 K; the hydrogen absorption rate of Specimen B became higher again than that of Specimen A after the heat treatment at 873 K.

The comparatively small hydrogen absorption rate observed for the as-prepared Specimen B can be ascribed to (1) small hydrogen permeability in NbC, and/or (2) presence of oxide layers at Pd/NbC interface. As described above, the Pd films were prepared in the different vacuum apparatus, and hence the oxide layers formed during the specimen transfer have to be removed by vacuum heating prior to the preparation of Pd films. It is, however, known that the diffusion rate of oxygen in NbC is significantly smaller than that in Nb [16]. Hence, it is plausible that the oxide films could not be fully removed under the present conditions. As described in the previous paper [13], a pure Nb specimen also showed a small hydrogen absorption rate in the as-prepared conditions after recrystallization annealing to

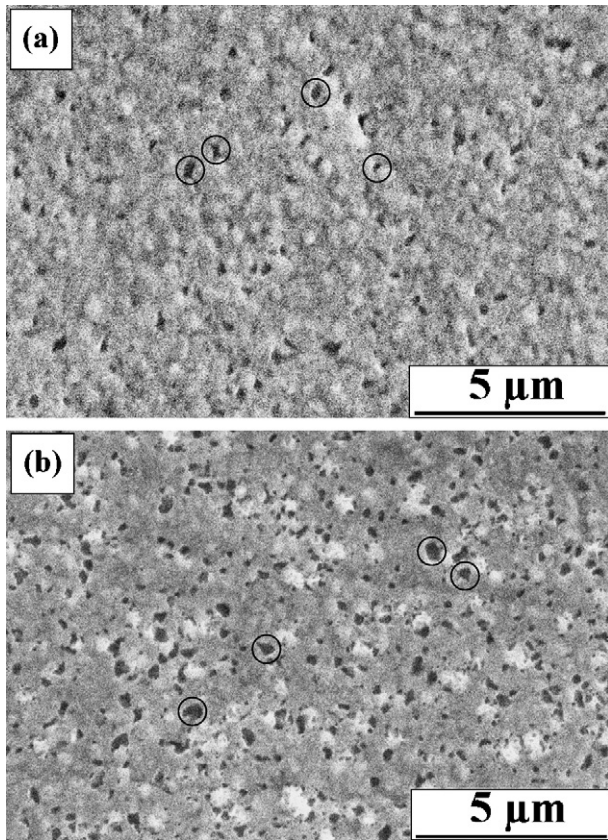


Fig. 2. Typical examples of SEM image of Specimen B after hydrogen absorption experiments subsequent to heat treatments in vacuum at 773 K (a) and 873 K (b). Some open pores are indicated by circles as examples.

remove defects. Therefore, the influence of oxide layers beneath the Pd films has to be carefully examined in order to clarify the mechanism underlying the comparatively small hydrogen absorption rate in the as-prepared conditions. For this purpose, a new vacuum apparatus is under construction at the present to prepare Pd films after carburization without exposure to air.

The morphology of Pd films of Specimen B was observed by means of SEM after the heat treatments at 773 and 873 K to understand the mechanism underlying the sharp reduction and recovery in hydrogen absorption rate (Fig. 1(b)). Fig. 2 shows typical examples of SEM images of Specimen B after hydrogen absorption experiments subsequent to the heat treatments at 773 K (a) and 873 K (b). Circles in these figures indicate some of the open pores as examples. It is obvious that the extent of porosity development in the Pd films increased monotonously with heat treatment temperature. As described above, the hydrogen absorption rates of Specimen A and the specimens without intermediate layer [13] decreased with increasing extent of porosity development due to the formation of Nb oxides by the exposure to air after heat treatments. Such correlation does not hold in this case. In addition, XRD analyses showed that Pd remained in its crystal structure after the heat treatments at 773 and 873 K; no noticeable loss of Pd due to the formation of intermetallic compounds with or dissolution in Nb was observed. Fig. 3 shows a typical XRD pattern obtained after the heat treatment at 773 K. The peaks of Pd are clearly observed in this figure.

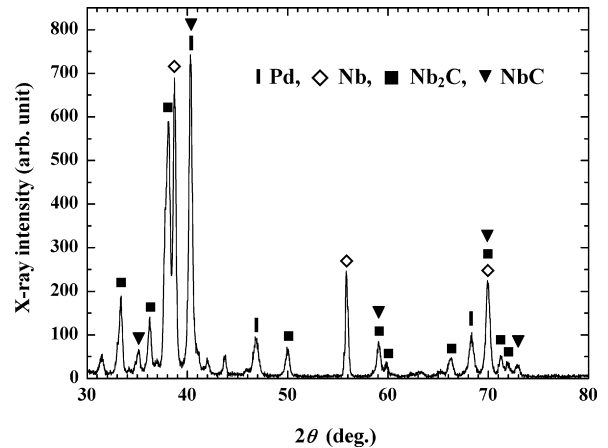


Fig. 3. Typical XRD pattern of Specimen B after hydrogen absorption experiment subsequent to heat treatment in vacuum at 773 K. The incident angle of X-rays (Cu  $K\alpha$ ) to the specimen surface was adjusted to be  $3^\circ$ .

For comparison, Specimen B was subjected to similar hydrogen absorption experiments at 573 K but without exposure to air; the specimen was kept in vacuum ( $10^{-4}$  Pa) at room temperature for 1 h (3.6 ks) after the heat treatments instead of the exposure to air. In this case, the extent of reduction in hydrogen absorption rate was significantly smaller than that in Fig. 1(b). Typical results are shown in Fig. 4. The hydrogen absorption rate after heating at 773 K for 4 h (14.4 ks) was comparable for that after heating at 673 K for 1 h in Fig. 1(b). No observable change in hydrogen absorption rate was induced by additional heating at 873 K for 3 h (10.8 ks). The significant degradation in the coating effect appeared only after subsequent heating at 973 K for 1 h (3.6 ks); the reduction in hydrogen absorption rate was ascribed to poisoning effects of water vapor present as residual gas in vacuum chamber and impurity in the hydrogen gas. These observations indicate that the coating effect of Pd was not severely degraded even after heating at 773 K, and oxygen taken up during the exposure to air plays an important role in the sharp reduction in hydrogen absorption rate (Fig. 1(b)). The slight reduction in hydrogen absorption rate after the heat treatment at 673 K in

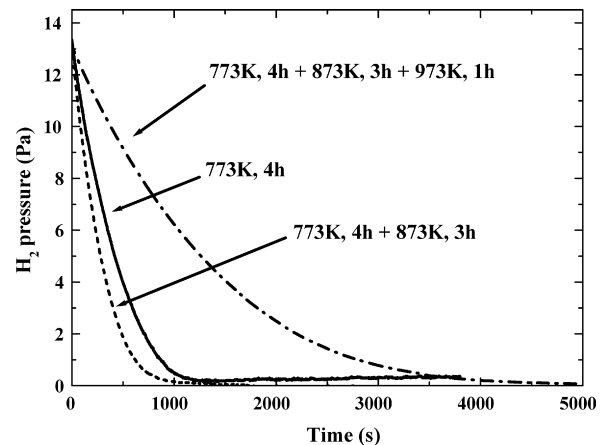


Fig. 4. Typical hydrogen absorption curves obtained for Specimen B at 573 K. The specimen was not exposed to air after heat treatments in vacuum at temperatures given in the figure.

Fig. 1(b) indicates that the development of open porosity already started at this temperature, and the following exposure to air at room temperature resulted in the formation of Nb oxides in the bottoms of such open pores. It is plausible that oxygen in the Nb oxides diffused along Pd/NbC interface of non-porous regions during subsequent heat treatment at 773 K. The contamination of Pd/NbC interface by oxygen should result in the decline in penetration rate of hydrogen from Pd to NbC and consequently induce the sharp reduction in hydrogen absorption rate. The diffusivity of oxygen in NbC is radically smaller than that in Nb as mentioned above [16], and hence dissolution of oxygen into Nb bulk should be retarded by the NbC layer at 773 K. The recovery in hydrogen absorption rate by heating at 873 K can be attributed to the enhancement of oxygen diffusion through the NbC layer to the bulk of Nb; the activation energy of oxygen diffusion in NbC has been reported to be 145 kJ/mol [16]. Further investigation, however, is necessary for the full clarification of the mechanism underlying such complicated temperature dependence.

In the most cases, the hydrogen permeability of composite membranes is investigated by continuous experiments with highly pure hydrogen gas. Oxygen, however, is present in membrane reactors as, for example, H<sub>2</sub>O, CO and CO<sub>2</sub> in the case of steam reforming of hydrocarbons. In addition, membranes could be exposed to air during maintenance works. The present results strongly indicate the importance of examination on influence of oxygen.

#### 4. Conclusions

Non-porous intermediate layers comprising NbC and Nb<sub>2</sub>C were prepared between thin Pd films and Nb substrates, and their effects on the high temperature stability of Pd films were examined by the heat treatments from 573 to 873 K followed by the exposure to air at room temperature and hydrogen absorption experiments at 573 K. This type of intermediate layer provided better stability of Pd films than the layers consisting solely of Nb<sub>2</sub>C after the heat treatments at/below 673 K. The hydrogen absorption rate showed complicated behavior in the higher temperature region, whereas the extent of porosity development in Pd films monotonously increased with temperature. Namely, sharp reduction and recovery in hydrogen absorption rate were

observed after the heat treatments at 773 and 873 K, respectively. The extent of reduction in hydrogen absorption rate by heat treatments at 773 K was significantly smaller when the specimen was not exposed to air. Hence, the complicated temperature dependence observed was attributed to the influence of oxygen taken up through open pores during the exposure to air.

#### Acknowledgements

This study was supported in part by a Grant-in-Aid for Scientists Research (C) of Ministry of Education, Culture, Sports, Science and Technology of Japan, No. 17560613. The authors express their sincere thanks to Professor K. Ikeno of University of Toyama for use of SEM.

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