

# Study of hydrogen diffusion in Nb–Ta alloys by Gorsky effect measurement

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## Abstract

Hydrogen diffusion in  $\text{Nb}_x\text{Ta}_{1-x}$  alloys ( $x=0, 0.1, 0.25, 0.5, 0.75, 0.9$  and  $1.0$ ) was investigated over a temperature range between 160 and 340 K by measurements of the Gorsky effect. The temperature dependence of the hydrogen diffusivity,  $D$ , of specimens with  $x=0, 0.9$  and  $1.0$  showed a deviation from the Arrhenius type behavior at low temperatures, while the other alloys did not show such a deviation. The value of  $D$  decreases with alloying at both the Nb- and Ta-rich ends and exhibits a minimum at  $x \simeq 0.50$ . The concentration dependence of  $D$  is stronger at the Nb-rich end than that at the Ta-rich end. The hydrogen potential obtained by a first-principles calculation shows that a Ta atom acts as a trapping center for hydrogen in the Nb matrix and a Nb atom acts as an anti-trapping center in the Ta matrix. It is concluded that the main reason for the decrease in  $D$  is different for the Nb-rich and Ta-rich alloys: the hydrogen trapping for the former and a disturbance of tunneling jump for the latter.

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## 1. Introduction

Hydrogen diffusion has been extensively investigated in many alloys. It is interesting to note that the dependence of the hydrogen diffusivity,  $D$ , on the alloy concentration is different for different alloy systems. Barlag et al. [1] summarized the experimental results for various fcc palladium alloys as follows. When Pd is alloyed with elements with lower hydrogen solubility, e.g. Ag, Ni and Cu,  $D$  essentially remains constant up to alloy concentration of 25% and then decreases steeply by about three orders of magnitude. On the other hand, when alloyed with elements with higher hydrogen solubility, e.g. V and Nb,  $D$  decreases rapidly with the alloy concentration. They explained that Ag, Ni and Cu atoms block the hydrogen path in the Pd matrix and V and Nb atoms act as trapping centers for hydrogen. For fcc Pd alloys, it is also worthwhile to note that  $D$  slightly increases with the alloy concentration when elements with a large atomic radius [2,3], e.g. Ce and Y, are chosen. The expansion of the lattice is considered to be responsible for the enhancement of the diffusion.

The hydrogen diffusion in bcc alloys is somewhat different from that in fcc alloys. Peterson and Herro [4] investigated the composition dependence of  $D$  in the Nb–V system and found that  $D$  decreases rapidly with solute concentration at both ends and exhibit a very deep minimum at 75% Nb. It is interesting to note that there is no indication of diffusion enhancement in V-rich alloys although the Nb atom is 10% larger than the V atom.

In this work we have investigated the hydrogen diffusion behavior in the Ta–Nb system. Ta and Nb have similar properties both in the elastic and electronic nature. The diffusivity of hydrogen in Nb at room temperature, however, is almost one order of magnitude larger than that in Ta. We measure the diffusivity of the Nb–Ta system over the whole range of the alloy concentration by the Gorsky effect method. We will discuss the experimental results in the light of the knowledge of the hydrogen potential obtained by a first-principles calculation.

## 2. Procedures

### 2.1. Specimen preparation

$\text{Nb}_x\text{Ta}_{1-x}$  ( $x=0, 0.1, 0.25, 0.5, 0.75, 0.9$  and  $1.0$ ) alloys were prepared by arc melting from starting materials of commercial purity (99.9%). The alloys were annealed for homogenization at

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Table 1  
 $\text{Nb}_x\text{Ta}_{1-x}$  specimens and the Arrhenius parameters of the diffusion coefficient of hydrogen around 300 K.

Composition $x$	Thickness (mm)	H content (at.%)	$(\Delta\rho/\Delta c)^a$ ( $10^{-9} \Omega \text{ m/at.}\% \text{H}$ )	$D_0$ ( $10^{-8} \text{ m}^2/\text{s}$ )	$Q$ (meV)
0	0.253	0.46	8.03	4.2	$136 \pm 3$
0.1	0.303	0.330	7.66	4.5	$140 \pm 3$
0.25	0.313	0.248	7.27	3.8	$146 \pm 6$
0.5	0.307	0.206	6.85	5.5	$165 \pm 5$
0.75	0.382	0.189	6.71	4.2	$140 \pm 6$
0.9	0.472	0.207	6.68	1.9	$100 \pm 7$
1.0	0.654	0.320	6.68	1.9	$91 \pm 6$

<sup>a</sup> The resistivity increment per 1 at.% hydrogen determined by Westlake and Miller [5].

1473 K for 12 h in a dynamic vacuum of  $10^{-4}$  Pa and then cold-rolled and cut out to strips of  $110 \text{ mm} \times 3 \text{ mm} \times (0.2\text{--}0.8) \text{ mm}$ . After chemical polishing, they were wrapped in zirconium foils and annealed at 1473 K for 12 h in an evacuated quartz tube so as to remove residual oxygen. The oxygen content of the Nb and Ta specimens were evaluated from the Snoek peak height to be less than 100 at. ppm. The strips were wound into coiled springs with a diameter of 12 mm and then loosely wrapped with zirconium foils and annealed at 1473 K for 12 h in a dynamic vacuum of  $10^{-4}$  Pa. Hydrogen of about 0.2 at.% was charged to the specimens electrolytically. The hydrogen content was determined from the increase in electrical resistivity during the hydrogen charging. The amount of hydrogen and the resistivity increase per at.%H,  $(\Delta\rho/\Delta c)$  [5], are summarized in Table 1.

## 2.2. Gorsky effect measurement

The Gorsky effect was measured by the elastic aftereffect method in an inverted torsion pendulum apparatus. The specimen was at first elastically deformed at a constant strain (about  $1 \times 10^{-4}$  in the maximum surface strain) for a period of about 2.5 times of the expected relaxation time and was then put into a stress-free condition. The strain of specimen was monitored by the optical lever method. During the elastic aftereffect mea-

surements, the temperature was controlled within  $\pm 0.5$  K. The relaxation process was almost a simple exponential function with a single relaxation time,  $\tau$ . The hydrogen diffusion coefficient,  $D$ , was determined by the relation [7]:

$$D = \frac{d^2}{\pi^2\tau}, \quad (1)$$

where  $d$  is the specimen thickness.

## 2.3. First-principles calculation

The hydrogen potential for dilute Nb-Ta alloys was calculated by a first-principles pseudopotential method using a computer program package “Osaka2002” developed by Shirai et al. [8,9]. A supercell of  $\text{A}_{15}\text{B}$  ( $\text{Nb}_{15}\text{Ta}$  and  $\text{Ta}_{15}\text{Nb}$ ) consisting of  $2 \times 2 \times 2$  bcc cells was relaxed so as to minimize the total energy, and the lattice parameter and the atomic positions were determined. The total energy of the supercell containing a hydrogen atom was then calculated. In the calculation the lattice was isotropically expanded by  $2.8 \times 10^{-30} \text{ m}^3$  in volume, which is the atomic volume of hydrogen, but to save the calculation time the atomic positions were not relaxed. Finally a hydrogen potential map was obtained for the atomic planes, which contain both the tetrahedral and octahedral interstitial sites. The cut-

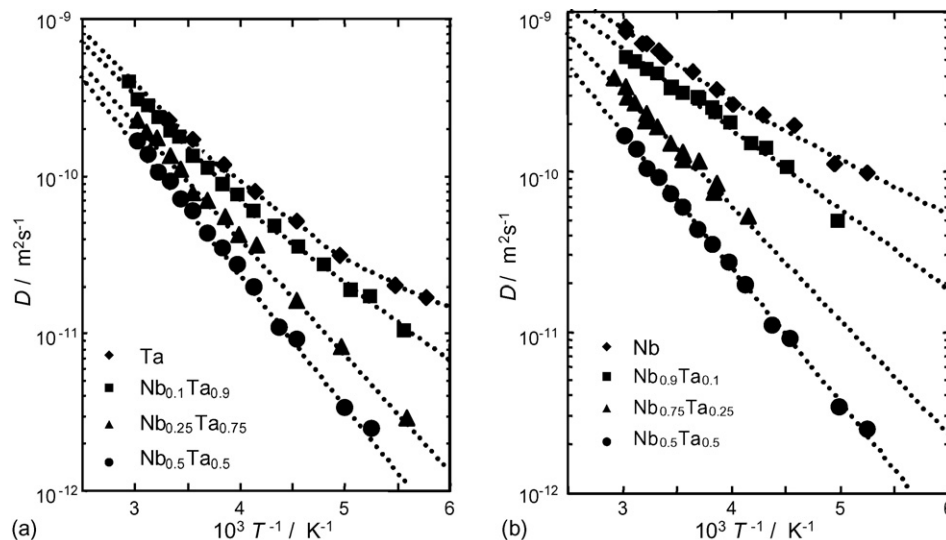


Fig. 1. Temperature dependence of hydrogen diffusion coefficient,  $D$ , in the Nb-Ta system. (a) Pure Ta,  $\text{Nb}_{0.1}\text{Ta}_{0.9}$ ,  $\text{Nb}_{0.25}\text{Ta}_{0.75}$  and  $\text{Nb}_{0.5}\text{Ta}_{0.5}$ . (b) Pure Nb,  $\text{Nb}_{0.9}\text{Ta}_{0.1}$ ,  $\text{Nb}_{0.75}\text{Ta}_{0.25}$ , and  $\text{Nb}_{0.5}\text{Ta}_{0.5}$ .

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