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A study of absorption processes of hydrogen isotopes in some transition metals by LiOD + LiOH mixture electrolysis

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Abstract

The concentration depth profiles of protium and deuterium in Ti, Nb and Ni loaded using LiOD + LiOH mixture electrolyte have been measured by means of ERDA and SIMS techniques. The isotope absorption ratios, deuterium/protium, determined by the ERDA measurement are estimated to be $(D/H)_{Ti} = 0.43$ and $(D/H)_{Nb} = 0.17$ while the content in Ni is below the detection limit. The agreement between the values determined by the ERDA and SIMS measurements is reasonably good. Based on the transport-absorption model, the mass balance equations have been developed and utilized for the present data analysis. This model reveals that the isotope absorption ratio for the Nb case is governed mainly by the flux of hydrogen ions flowing to the surface of the metal electrode, while for the Ti case the competition between the absorption–conversion process and the recombination process in the electrolysis becomes essentially important for the isotope absorption ratio. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The hydrogen absorption metals play an important role to develop the energy system without CO_2 release [1]. The suitable and safe handling of tritium is the most important problem for realization of the future nuclear fusion reactors because of its rather difficult chemical separation as well as radioactive treatment. The hydrogen absorption metals are also applied for the isotope separation techniques and the study of hydrogen brittleness [2–4]. It is therefore primarily important to understand the basic characteristics of the absorption of hydrogen isotopes in some transition metals.

In the present work, the systematic experiments were performed to study the lattice structure dependence of the hydrogen isotope absorption processes in each metal. The absolute quantities of protium and deuterium were measured by elastic recoil detection analysis (ERDA), and the depth profiles were also analyzed by secondary ion mass spectrometry (SIMS).

In the previous study, we proposed an electrolysis model for hydrogen isotopes absorption processes in metal and discussed about the dominant reactions in the electrolysis using the solution of a set of the mass balance equations [5]. The solution reasonably explained the electrolysis processes in the Zr and Pd cases. We therefore employ the model to analyze the present data obtained in the experiments on other transition metals. The hydrogen isotope absorption ratios for the metals are closely related to their lattice structures as

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well as the transport-reaction processes occurring in the electrolysis.

2. Experimental

2.1. Experimental setup

The experimental setup was described in details in the previous report [5].

The Ti, Nb, and Ni specimens were employed for the present experiments. All the specimens were supplied by Nilaco. The size of all specimens was 10 mm × 25 mm. The thickness of each specimen was 1.0 mm. The purity and the amount of major impurities are listed in Table 1. All the samples were polished mechanically and annealed at 973 K for 10 h in vacuum of around 10^{-7} Torr. The ion-exchanged water was used as the light water and the heavy water was purchased from Isotec. The isotope purity of deuterium was 99.9%. All of them were used after the distillation with potassium permanganate.

The hydrogen isotopes were charged to the samples electrolytically for one day with the current density of 800 mA/cm^2, which was controlled within the ambiguity of 1%.

2.2. The estimation of the quantities of protium and deuterium by ERDA

The depth profiles of protium and deuterium loaded in the specimens were measured by means of the ERDA technique at Nagoya University, where 1.7 MeV He$^+$ ion was incident on the specimen at the angle of 80° to the surface normal and H$^+$ and D$^+$ ions recoiled at the forward angle of 80° to the surface normal, were detected by the SSD semiconductor detector [6,7]. The fluence of He$^+$ ions bombarded on the specimen during the ERDA measurement was monitored simultaneously by means of the RBS measurement.

The concentrations of protium and deuterium absorbed were calibrated using the data for graphite reference material [8,9]. The typical values for calculating the average stopping cross sections of $[\varepsilon]^{\mathrm{Me}}_{\mathrm{ERD}}$ and $[\varepsilon]^{\mathrm{Me}}_{\mathrm{RBS}}$ were obtained by the theoretical equations in Refs. [10,11], which are summarized in Table 2. The values of the cross sections employed for protium and deuterium at 1.9 MeV were cited from Ref. [12].

2.3. The depth profiles of protium and deuterium by SIMS measurement

The depth profiles of protium and deuterium were measured with a SIMS at Tokyo Institute of Technology. The sputtering beam was 15 keV O_2^+ ions and the beam current was 4×10^{-7}A. The Dektak profilometer measurements give a sputtered thickness of the specimens. The depth scale was calculated by the sputtering time and the sputtered thickness. The resolution of H_2^+ and D$^+$ were checked before the measurements [5]. Then, the sputtered depth was estimated to be 2 μm.

3. Results

3.1. The loading ratio estimation of protium and deuterium by ERDA measurement

The RBS spectra for all the metals attained during the ERDA measurements are shown in Fig. 1. The peak in about 875 channel in Fig. 1 corresponds to platinum, which is used as anode. This result implies that the small amount of this impurity is deposited on the cathode surface, but these amounts are not essentially considered to influence the hydrogen absorption processes. The

Table 1
The summary of the specimen conditions

	Ti	Nb	Ni
Purity (wt%)	99.9	99.7	99.7
Thickness (mm)	1.0	1.0	1.0
Typical imputiries (wt%)	0.30% Fe	370 ppm Ta	0.15% Mn

Table 2
Typical value of the stopping power and scattering cross section of the metals

	$[e]_{\mathrm{H,ERD}}$ (10^{-15} eV cm^2/atom)	$[e]_{\mathrm{D,ERD}}$ (10^{-15} eV cm^2/atom)	$[e]_{\mathrm{RBS}}$ (10^{-15} eV cm^2/atom)	$S_{\mathrm{scattering}}$ (E_0) (cm^2/Sr)
Ti	297.34	400.97	476.83	9.854×10^{-25}
Ni	307.62	411.95	476.76	1.603×10^{-24}
Nb	435.57	586.23	689.93	4.347×10^{-25}
C	123.33	–	105.17	6.036×10^{-26}

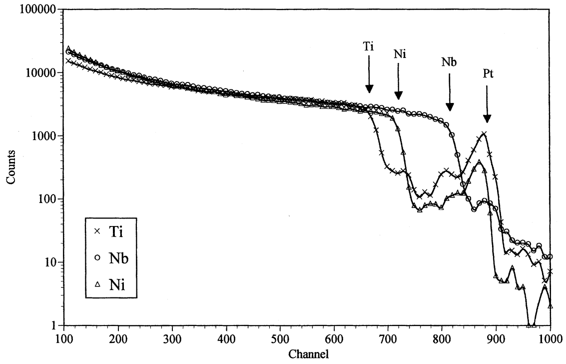

Fig. 1. The RBS spectra of 1.7 MeV He$^+$ ion beam from specimens with simultaneous electrolysis.

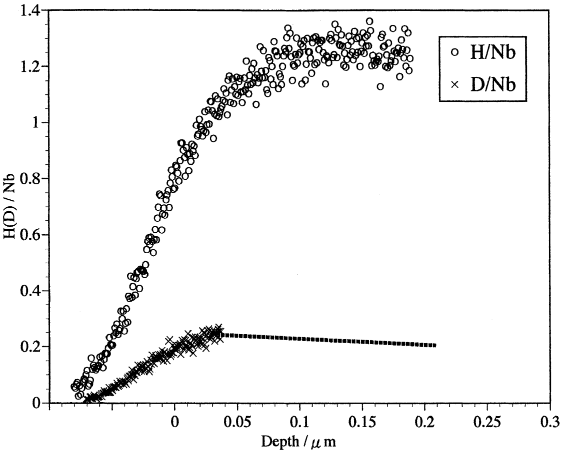

Fig. 3. The depth profiles of the D (○) and H (×) loaded in Nb by simultaneous electrolysis.

loading ratios, H/M and D/M in metals of Ti, Nb and Ni measured by the simultaneous electrolysis are shown in Figs. 2–4, respectively. The method for calculating the hydrogen loading ratio from the ERDA spectra was the same as the method described in Ref. [2]. In these figures, the depth profiles were converted from the ERDA spectra of H and D. The dotted lines are the overlapping tails of the ERDA spectra of D which separated from the experimental ERDA spectra by subtraction of the ERDA spectra of H assumed.

Fig. 2 depicts that the amounts of H and D loaded in Ti by the simultaneous electrolysis increase steeply at the surface and reach the saturated levels of about 0.70 and 0.30, respectively, with increasing the depth. The amounts of H and D loaded in Nb by the simultaneous electrolysis shown in Fig. 3 are seen to be 1.20 and 0.30. The isotope absorption ratios in Ti and Nb by the simultaneous electrolysis are calculated to be 0.43 ± 0.13 and 0.17 ± 0.05, respectively. The loading ratio of hydrogen isotopes in these metals by the separate electrolysis are 1.00 and 0.66, respectively. In the case of Zr, those were also 0.60 and 0.20, respectively [5]. In the case of Nb, however, the loading ratio of D (= 1.70) in nearly equal to that of H (= 1.80). The isotope absorption ratios in Ti and Nb by the separate electrolysis are calculated to be 0.66 and 0.94, respectively which are quite different from those by the simultaneous electrolysis.

The isotope absorption ratios in Ni could not be evaluated from the ERDA spectra, because the amounts of H and D loaded were very small, as seen from Fig. 4. Based on these experimental results, the absorption property for the metals can be classified into two groups. The first group is the case that the isotope absorption ratio by the separate electrolysis is almost unity and the

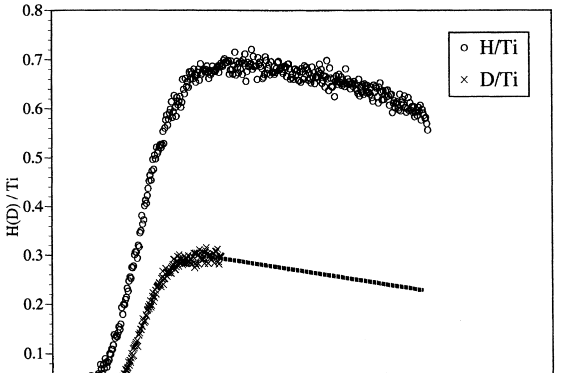

Fig. 2. The depth profiles of the D (○) and H (×) loaded in Ti by simultaneous electrolysis.

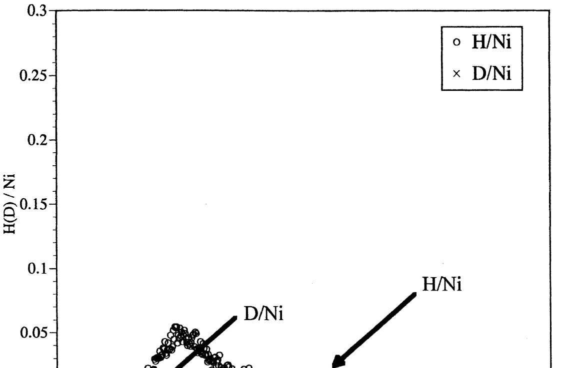

Fig. 4. The depth profiles of the D (○) and H (×) loaded in Ni by simultaneous electrolysis.

second group is the case that the isotope absorption ratio is less than unity, namely the loading ratio of D is smaller than that of H and the isotope absorption ratio in the second group by the simultaneous electrolysis is larger than that in the first group.

3.2. The depth profiles of protium and deuterium by SIMS measurement in deep layer

As is commonly known, the profiling achieved by ERDA is limited to the depth of somewhat 0.3 μm. To obtain the concentration profile in deeper layers of specimens, the SIMS measurements were performed in the present study. Fig. 5 shows the depth profiles of protium and deuterium loaded in Ti, Ni and Nb by simultaneous electrolysis. Vertical data points for hydrogen are normalized by the bulk concentration of metals. The depth profiles indicate that protium and deuterium are uniformly absorbed in all the specimens. The amount of the protium and deuterium in Ni were much smaller than those in all the other specimens and were almost equal to the background level. The last fact suggests that the protium and deuterium were not accumulated in Ni specimen. From these experimental results, the depth dependences of the isotope absorption ratios are plotted in Fig. 6. The isotope absorption ratios are seen to keep almost constant within 1 μm. The isotope absorption ratios picked up at the position of 0.5 μm are summarized in Table 3. The isotope absorption ratios in Ti and Nb measured by the SIMS technique are found to be somewhat smaller than those measured by the ERDA technique. The difference may be ascribed partly to ambiguity in subtraction of the overlapping tails of the ERDA spectrum of D and also the ionization probability of H and D in the SIMS analysis.

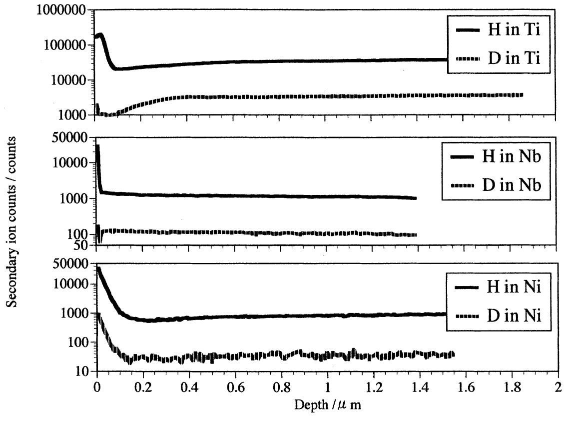

Fig. 5. The depth profiles of H^+ and D^+ ions by use of O_2^+ ions as primary ions in SIMS.

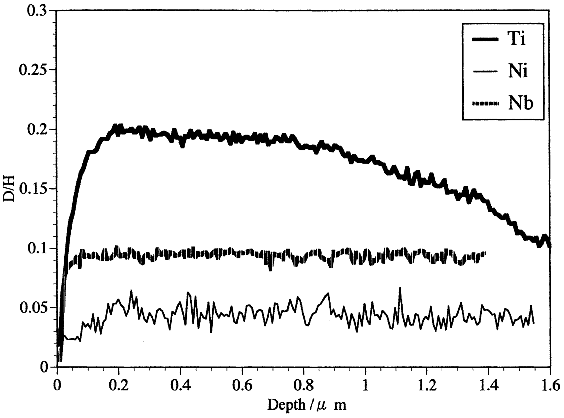

Fig. 6. The depth profiles of hydrogen isotope ratios in metals determined by SIMS.

4. Discussion

In the preceding section, the absorption ratios of hydrogen loaded in various metals by the separate and simultaneous electrolysis were determined by the ERDA and SIMS measurements. We discuss the results using the mass balance equations which were explained basically in Ref. [5].

In the case of Nb, the absorption ratio of D to H loaded by the separate electrolysis is close to unity. This fact indicates that the isotope absorption ratio is controlled by the current density. Thus in this case, the amounts of H and D absorbed are mainly determined by the fluxes of the ions reaching the specimen surface in the electrolysis. The isotope absorption ratio in Nb loaded by the simultaneous electrolysis was found to be 0.17 ± 0.05 by the ERDA measurement. The isotope absorption ratio of D to H by the SIMS measurement has been also estimated to be 0.09. These values are close to the hydrogen isotope ratio of the ionization quotient in waters [13–16]. These results suggest that the isotope absorption ratio in Nb is controlled mainly by the flux ratio, such as in Pd which was studied in our previous paper [5].

In the Ti case, the isotope absorption ratio of D to H loaded by the separate electrolysis was not unity and this result could not be explained only in terms of the ion fluxes reaching the specimen surface. This is the recombination-controlled case, in which the amounts of H and D absorbed are mainly determined by competition between the absorption and recombination processes. The isotope absorption ratio in metals loaded by the separate electrolysis can be described in terms of $\left(\xi_{\mathrm{ab}}^{\mathrm{D}}/\xi_{\mathrm{ab}}^{\mathrm{H}}\right)\left(\sqrt{K^{\mathrm{HH}}/K^{\mathrm{DD}}}\right)$ using the mass balance equations, where $\xi_{\mathrm{ab}}^{\mathrm{D}}$ and $\xi_{\mathrm{ab}}^{\mathrm{H}}$ are the absorption rate constants of D and H, respectively, and K^{DD} and K^{HH} are the recombination rate constant of D–D and H–H at the

Table 3
The results of ERDA, SIMS and calculation

	Ti	Nb	Ni
ERDA measurement			
Separate electorlysis			
H/Me	1.00	1.80	<0.02
D/Me	0.66	1.70	<0.01
D/H	0.66	0.94	–
Simultaneous electroysis			
(H + D)/Me	1.00	1.40	–
H/Me	0.70	1.20	<0.02
D/Me	0.30	0.20	<0.01
D/H	0.43	0.17	–
SIMS measurement			
Simultaneous electroylsis			
D/H	0.20	0.09	0.05
Calculated value			
Simultaneous electrolysis			
D/H	0.32	0.11	–

surface. The experimental value of the isotope absorption ratio was estimated to be 0.66 for Ti, loaded by the separete electrolysis. Using $\phi_{D^+}/\phi_{H^+} = 1$ the value of $(\xi_{ab}^{D}/\xi_{ab}^{H})(\sqrt{K^{HH}/K^{DD}})$ is determined from the experimental value of 0.66. Using the experimental ratio of $(\xi_{ab}^{D}/\xi_{ab}^{H})(\sqrt{K^{HH}/K^{DD}})$ and $\phi_{D^+}/\phi_{H^+} = 0.1$ and assuming $A = (K^{HD})^2/K^{HH}K^{DD} = 1$, the isotope ratio for Ti can be theoretically estimated to be 0.32. Thus we conclude that the theoretical value for Ti is reasonably consistent with the experimental ones by ERDA and SIMS techniques.

5. Conclusion

The ERDA and SIMS measurements of the concentration depth profiles of H and D were performed for Ti, Nb and Ni loaded using LiOD + LiOH mixture electrolyte. The absolute amounts of protium and deuterium absorbed within 0.3 μm were determined from the ERDA measurement and the depth profiles of them in deeper layers were analyzed by the SIMS measurement. The isotope ratios for each metal were evaluated from the experimental results, and those of Ti and Nb with simultaneous electrolysis were 0.43 ± 0.13 and 0.17 ± 0.05, respectively. It was also found that the hydrogen isotope is not accumulated in Ni. The dominant reactions for governing the isotope ratios were identified from the solution of the mass balance equations. It is revealed from the experimental results, that the absorption-controlled process explains reasonably the loading ratio for Nb. The recombination-controlled process also explains the experimental results for Ti.

It is concluded that the theoretical values on the model of the absorption processes are reasonably consistent with the experimental results of Ti and Nb by ERDA and SIMS measurements.

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