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**Deuterium and helium retentions of V-4Cr-4Ti alloy used as first wall of breeding
blanket in a fusion reactor**

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Abstract

The deuterium and helium retention properties of V-4Cr-4Ti alloy were investigated by thermal desorption spectroscopy (TDS). Ion energies of deuterium and helium were taken at 1.7 keV and 5 keV, respectively. The retained amount of deuterium in the sample irradiated at 380 K increased with the ion fluence and was not saturated to fluence of up to 1×10^{23} D/m². For the irradiation at 773 K, 0.1% of implanted deuterium was retained at the highest fluence. For the helium ion irradiation at room temperature, three groups of desorption peaks appeared at around 500, 850, and 1200 K in the TDS spectrum. In the lower fluence region ($< 1 \times 10^{21}$ He/m²), the retained helium desorbed

mainly at around 1200 K. With increasing fluence, the amount desorbed at 500 K increased. Total amount of retained helium in the samples saturated at fluence up to 5×10^{21} He/m² and saturation level was 2.7×10^{21} He/m².

1. Introduction

Vanadium alloy is an attractive structural material used for fusion reactor because of its low induced radioactivity and good thermal and mechanical properties at high temperatures [1-5]. The vanadium alloy, V-4Cr-4Ti, may be a promising material because it shows excellent mechanical tolerance to neutron damage [2,3] and low helium and hydrogen production rate during 14 MeV neutron irradiation [5]. One of the important concerns regarding the vanadium alloy is its large retention of tritium (deuterium) caused by gas absorption and ion implantation. Even if there are many papers on hydrogen absorption, there are little data on the deuterium retention of vanadium alloy after deuterium (hydrogen) ion implantation [6]. The first wall of V-alloy is also exposed to helium ions with different energies during helium glow discharge cleaning and helium ash resulting from fusion reactions. Therefore, the interaction of helium with vanadium alloy has to be investigated after helium ion implantation. There are reports on the helium retention property for the vanadium and

vanadium alloy irradiated by helium ion but the fluence of helium ion was low ($\sim 10^{18}$ He/m²) [7,8].

In a previous study [9], the deuterium retention property of V-4Cr-4Ti alloy sample irradiated at 380, 573, and 773 K was investigated by using an Electron Cyclotron Resonance (ECR) ion irradiation apparatus [10] and thermal desorption spectroscopy (TDS). It was found that the deuterium retention property varied with different irradiation temperature, i.e. the amount of deuterium retained in the sample (here after, D-retention) irradiated at 380 K increased with the deuterium ion fluence and exceeded 100 % of the implanted deuterium at higher ion fluence. Whereas, D-retention at 573 K was almost the same irrespective of ion fluence, while for the case of 773 K, D-retention decreased at higher ion fluence. For this excessive D-retention (>100% trapping) irradiated at 380 K, two possible reasons were guessed. First reason was that deuterium desorbed from the chamber wall may have been included in the D-retention. Second reason was an enhanced absorption from the gas phase may have occurred during ion irradiation resulting in an overestimation of D-retention. In particular, the latter reason would be related to the reduction of surface impurity layer, which acts as the diffusion barrier of deuterium into the sample.

In this study, therefore, first we focused on the effect of deuterium desorption from

the chamber wall on the D-retention in the sample irradiated at 380 and 773 K. After deuterium ion irradiation, the irradiated sample was moved from the ECR ion apparatus to another TDS apparatus with an infrared image furnace and D-retention was measured. Second, in order to clarify the decrease in D-retention at higher ion fluence, the effect of surface impurity on the absorption amount during ion irradiation at 773 K was also investigated by using absorption apparatus.

In the present study, the helium retention property of V-4Cr-4Ti alloy sample was also examined by using the ECR ion irradiation apparatus. Helium ions were irradiated in the V-alloy at room temperature with high flux ($\sim 10^{18}$ He/m²/s) and high fluences (up to 1×10^{22} He/m²), i.e. this fluence corresponds to ~ 90 dpa in the projected range, which is comparable with that of α -particles of the operating condition of DEMO reactor. Subsequently, the retained deuterium or helium was measured by thermal desorption spectroscopy, TDS.

2. Experiments

V-4Cr-4Ti samples with low impurity contents [11], NIFS-HEAT-1 and 2, were prepared by National Institute for Fusion Science (NIFS). The sample size was 25 mm \times 5mm \times 0.25 mm. Before deuterium irradiation, the sample was mechanically

polished with Al₂O₃ powder and then degassed at 1273 K for 1hr in a vacuum of 10⁻⁶ Pa. After degassing, the sample was irradiated by deuterium ions at ~380 K (ambient temperature during ion irradiation) and 773 K (operation temperature of V-alloy blanket, 673~923 K [12]) with ion energy of 1.7 keV and higher ion fluence of 5~10 × 10²² D/m². The irradiated area was 10⁻⁴ m². The deuterium pressure during ion irradiation was 9×10⁻⁴ Pa. The D-retention in the sample was measured by using the TDS apparatus. The sample was heated from room temperature to 1273 K with a constant heating rate of 0.5 K/s by the infrared image furnace and was held at 1273 K for 60 min. The retained amount of deuterium was obtained by integrating the desorption rate for gases containing D over the heating time. Since the absorption of deuterium gas was observed during the ion irradiation, the absorbed amount was measured, i.e. the gas absorption experiment was conducted for the same sample at the same condition of ion irradiation, but without the ion irradiation. Consequently, the sample was resistively heated up to 1273 K and was held for 10 min in the ECR apparatus. Another experiment for absorption property of hydrogen gas was investigated by using the TDS apparatus with a constant volume of 1.3×10⁻³ m³ under different temperatures. Change of hydrogen pressure owing to absorption was monitored by a capacitance monometer.

For helium irradiation experiments, cold-rolled V-4Cr-4Ti alloy samples were used.

Before helium ion irradiation, the sample was heated at 1373 K for 1 hr in a vacuum of about 1×10^{-6} Pa and then was irradiated at room temperature (RT) by 5 keV helium ions. The fluence of helium ion was $(0.5-10) \times 10^{21}$ He/m², corresponding to 4.5 dpa (Fluence= 0.5×10^{21} He/m²)~91 dpa (1×10^{22} He/m²), comparable with that of α -particles of operating condition of DEMO reactor. Here the numbers of displacements per atom were average dpa-values in the projected range (27 nm) of 5keV-He ion. After helium ion irradiation, the sample was heated from RT to 1600 K with a heating rate of 1 K/s. The changes in surface morphology after ion irradiations were examined by scanning electron microscopy (SEM).

3. Results and discussion

3.1. Deuterium retention properties

The retained D atoms were desorbed as forms of D₂, HD, HDO, and D₂O in every sample. The main species desorbed from the irradiated sample was D₂. The fraction of D₂ gas to total amount of retained D into the sample was 90~95 %.

Fig.1

Fig.1 shows the amount of retained deuterium at temperatures of 380 K (a) and 773 K (b) as a function of deuterium ion fluence. The results obtained in the previous study are also plotted in this figure. In Fig.1, the amount of absorbed deuterium (q) is also

plotted as a function of gas fluences. The gas fluence means the number of incoming deuterium gas to the sample during ion irradiation.

Most of the deuterium retained and absorbed in the sample was desorbed by holding at 1273 K for 10 min. The amount of retained deuterium (Q-value) owing to ion implantation only was obtained by subtraction of the absorption amount of deuterium gas (q-value). The Q-value in the sample irradiated at 380 K increased with the ion fluences and exceeded 100 % of the implanted deuterium at a higher fluence even if the TDS measurement was conducted by using different apparatus. Accordingly, this result indicated that deuterium desorbed from the chamber wall was negligible. Similar result (100% trapping) was observed in titanium after deuterium ion implantation at RT by nuclear reaction analysis [13]. For 100 % trapping of deuterium in the titanium, it was suggested that the implanted D is distributed over the whole bulk of the titanium having high diffusion coefficient and high solubility of hydrogen as soon as the implanted range distribution becomes saturated [14]. The present result also suggests that the implanted D atom diffuses beyond the projected range to the bulk during ion irradiation. Vanadium hydride together with other metal hydride might have been formed in the near surface region. Assuming that all of the implanted D at ion fluence of 5×10^{22} D/m² was uniformly retained in the projected range (R_p) of 21 nm or the penetration depth

(λ_p) of 71 nm of pure vanadium, the deuterium concentrations (D/V ratio) in the R_p and λ_p would be 42.0 and 12.4, respectively. Here the depth of λ_p was the maximum depth in implanted region and the depth of R_p and λ_p of pure vanadium was obtained by the TRIM code and the number of vanadium atoms in the R_p and λ_p was estimated from the interplanar spacing of 0.3 nm and density of 5.87 g/cm³ for pure vanadium. These values were too large even if the hydride was formed within the depth of R_p and λ_p . In addition, no blister was observed on the surface in any sample. Therefore, it was presumed that deuterium could diffuse at least in the depth of more than ~ 440 nm in the irradiated sample at 5×10^{22} D/m² if vanadium hydride with the concentration (D/V) of 2.0 (VD₂) is formed in the sample. However, excessive trapping at higher fluence (> 100 % trapping) could not be explained. This result could imply that enhanced gas absorption might have occurred during ion irradiation, discussed below. In the surface region of the sample after degassing at 1273 K, titanium oxide with thickness of ~5 nm as a diffusion barrier of deuterium absorption was formed together with the impurity layer containing oxygen and carbon with ~30 nm. [9]. At ion fluence of 1×10^{22} D/m² (smallest fluence) and 1×10^{23} D/m² (largest fluence), the removed thickness owing to sputtering was calculated to be ~3.5 nm and ~35.4 nm, respectively by using sputtering yield (0.02) of pure V [15]. These calculated results mean that these impurity layers and

Ti-oxide were partially or totally removed at higher fluences. Therefore, the absorption rate might be strongly affected by deuterium ion fluence, i.e. the amount of absorbed deuterium might not be proportional to the gas fluence. The $q_{380\text{ K}}$ value increased with the gas fluence and sharply rose at highest gas fluence as shown in Fig.1 (a). This denoted that the surface state of the V-alloy sample had changed during ion implantation and following TDS measurement. At higher ion fluence, the absorption rate of deuterium gas might be intensified during ion implantation because of removal of the Ti-oxide and impurity layer. The irradiated sample was heated up to 1273 K to measure the Q-value. During this TDS measurement, Ti-oxide was again formed on the surface so that the absorption rate of D_2 gas during q-value measurement was reduced compared during ion implantation. We called this phenomenon as “enhancement of deuterium absorption during ion implantation”. This trend complicated the evaluation of the amount of absorbed deuterium during ion implantation. This enhancement of deuterium absorption resulted in an overestimation of deuterium retention owing to ion irradiation only (Q-value).

At the irradiation temperature of 773 K, the amount of retained deuterium ($Q_{773\text{ K}}$) was two orders of magnitude smaller than that irradiated at 380 K and further decreased at the highest fluence (Fig.1 (b)). The retained amount of deuterium diminished with

increasing irradiation temperature because the release of implanted D atoms became large at 450 K [9] and the solubility of deuterium in the V-alloy decreased [15]. The q_{773K} values slightly increased with the gas fluence. The equilibrium concentration of hydrogen (C_{eq}) under the condition of this study (9×10^{-4} Pa, 773 K) was extrapolated to be 0.23 wppm by using Sieverts' law and hydrogen solubility of the V-alloy [16]. The q_{773K} values were larger compared with the C_{eq} . This result indicated that the sample was not uniformly heated during both ion irradiation and absorption measurement because sample was resistively heated by switching on electric current.

Fig.2 shows the change of hydrogen gas pressure in another absorption chamber (volume= 1.3×10^{-3} m³) with the infrared image furnace for the annealed sample at 1273 K and Ti-oxide coated V-4Cr-4Ti alloy as a function of heating time changed from 473 K to 873 K. Here, the initial hydrogen gas pressure was 10 Pa. Titanium oxide layer with thickness of 200 nm was coated on all surfaces of the V-4Cr-4Ti alloy by reactive magnetrons sputtering. It could be seen that at lower temperature region (<573K), the Ti-oxide layer acted as a diffusion barrier of hydrogen gas. At 773 K after H₂ gas introduction in the adsorption chamber, the pressure decreased rapidly and became constant in the V-alloy sample with and without the Ti-oxide layer. This result means that hydrogen gas was easily absorbed into the V-alloy through the Ti-oxide layer. In

Fig.2

addition, the equilibrium concentration of hydrogen for the Ti-oxide coated sample was the same as that for degassed sample [16]. These results signified that the amount of absorbed deuterium in the sample during ion implantation at 773 K was not dependent of the surface state and was consistent with that of the q_{773K} value (Fig.1 (b)). The decline in Q_{773K} value was reproducibly observed. The latter event could be explained as follows: deuterium ion implanted in a clean surface region was hardly retained at higher fluence because the impurity layer having many lattice defects was sputtered at higher fluences. The retained amount of the implanted deuterium was 3~0.1%, which was comparable to graphite and tungsten [17]. Here, the amounts of graphite and tungsten at 773K were the values extrapolated from the data in reference [17].

The surface morphologies of the samples were observed before and after deuterium ion irradiation in every irradiation temperature. No significant change in surface morphology was found, i.e. no blister was formed on the sample. This result might clarify the diffusion of implanted deuterium beyond the projected range of 1.7 keV-D ion during ion irradiation.

3.2. Helium retention properties

Fig.3 shows SEM photographs of the irradiated sample with the fluence of 5×10^{21}

He/m² (45 dpa) (a), after heating up to 673 K in vacuum (b), and after heating at 1473 K (c) after helium ion irradiation at RT. A lot of blisters were observed on the irradiated sample, but the size and distribution of the blisters were not uniform. The blister size ranged from 0.1 to 0.5 μm and large blisters were observed in some areas. The densities of the large blister (0.3~0.5 μm) and the small blister (~0.1 μm) were (8~9)×10¹²/m² and 2×10¹³/m², respectively. Since the sample was re-crystallized by pre-annealing treatment at 1373 K, the structure of grains appeared on the sample. Therefore, the distribution of the blister might correspond to the difference in grain property, such as crystal orientation [18]. Some of the blisters were exfoliated as shown in the parts enclosed with circles. After heating at 673 K, no significant changes were observed on the surface. However, after heating at 1473 K, many blisters ruptured and pinholes were observed. The density and the size of the holes caused by rupture were approximately 6×10¹² /m² and 0.1~0.5 μm, respectively. The ratio of the heating temperature (T=1200~1473K) to the melting point (T_M), T/T_M, was 0.56~0.68, which was very similar to T_{irrad}/T_M ratio (>0.5) for the pinhole formation during helium ion irradiation [19].

Fig.3

Thermal desorption spectra of helium of the V-alloy are shown in Fig.4. Several desorption peaks were observed in the TDS spectra. These peaks were divided into three

Fig.4

groups. Peak I was the desorption around 500K, Peak II at 826~896 K, and Peak III at temperature higher than 1100 K. The activation energies (E) for Peak I, II, and III were estimated by using Readhead's equation of first-order desorption [20].

$$E = RT_p \left(\ln \frac{T_p v_1}{\beta} + \ln \frac{1}{\ln \frac{v_1 T_p}{2\beta}} \right) \quad (1)$$

Here, R is gas constant, T_p peak temperature, β heating rate (=1K/s). Attempt frequency (v_1) is assumed to be 10^{13} s^{-1} [20,.21].

The activation energies of Peak I, II, and III were obtained as 1.50, 2.35~2.59, and 3.59~4.16 eV, respectively. It was reported that the dissociation energies of He_nVX type defect cluster and $\text{He}_n\text{V}_5\text{X}$ cluster for the V and other V-alloy were ~1.5eV and ~2.48 eV [21]. Here, n denoted the number of helium atom ($n>1$), V vacancy, and X impurity atoms, such as C, N, or O. The blister with a size larger than sub-micron did not rupture after heating at 673 K as shown in Fig.3 (b). This result seemed to support the desorption at around 500 K corresponding to the dissociation of He_nVX type defect cluster. Since the rupture temperature of the blister and internal bubbles changed with the blister size, multiple peaks appeared in the high temperature region ($>1200\text{K}$). Then it was conceived that the helium desorption of Peak III corresponded to the rupture of the blister and internal bubbles.

Fig.5 shows the total amount of retained helium in the V-alloy. The amounts corresponding to Peak I, II, and III are also shown in Fig. 5. The amount of retained helium of Peak III and II was saturated at low fluence, while that of Peak I was gradually saturated at higher fluence. This was contrary to the phenomenon observed in the pure V and V-alloy irradiated with low fluence of 10^{18} He/m² [7], in which the amount of desorbed helium from the He_nVX type defect cluster (~550 K) was saturated at low fluence ($\sim 10^{18}$ He/m²). The impurity layer containing oxygen and carbon was removed by helium ion in the present study. The sputtered depth was 0.48 nm (Fluence= 5×10^{20} He/m²) ~ 9.5 nm (1×10^{22} He/m²). The contribution of the He_nVX type defect cluster might be smaller with ion fluences due to the decrease in impurity concentration in the near surface region. However, the retained amount of Peak I increased with ion fluence. One possible reason was that the desorption from trapped helium in vacancies produced by helium ion such as He_mV ($m \gg 1$) was also contained in Peak I. Nevertheless, this remains to be an open question and further investigation by using TEM is necessary.

Helium concentration within the depth of the projected range (27nm) of 5 keV He⁺ ion was estimated by using pure vanadium's data. Helium concentrations (He/V) at the saturation levels of Peak I, II, and III were approximately 0.7, 0.08, and 0.7, respectively.

Total amount of retained helium corresponded to 1.4 of He/V. The total amount of retained helium was saturated at the fluence of $\sim 5 \times 10^{21} / \text{m}^2$ and the value was $2.75 \times 10^{21} \text{ He} / \text{m}^2$. It has been reported that the origin of the bubble and blister was He_nVX [21]. Therefore, if the V-alloy would be kept at operational temperature during both discharge cleaning and ion implantation, the amount of desorbed He for the Peak I would significantly decrease and the amount of retained He would be small.

4. Conclusion

The deuterium and helium retentions of the V-4Cr-4Ti alloy were investigated by using an ECR ion irradiation apparatus and TDS. The retained amount of deuterium due to ion implantation significantly depended on the irradiation temperature. In irradiation with temperature of 380 K, no saturation of retained amount was observed in the present irradiation condition. Whereas, in the irradiation at 773 K (operating temperature of the V-alloy blanket), the retained amount increased with the fluence but dropped at the fluence of $10^{23} \text{ D} / \text{m}^2$. In this case, 0.1% of implanted deuterium was retained, which was comparable to other plasma facing materials, such as graphite and tungsten.

A lot of blisters with a diameter of 0.1~0.5 μm were observed after helium irradiation at room temperature. Total amount of retained helium was saturated for the

fluence higher than 5×10^{21} He/m² and the saturation value was 2.7×10^{21} He/m², corresponding to 1.4 He/V.

Desorption and retention behaviors of deuterium and helium examined in this study could be useful for wall conditionings of first wall of the V-alloy for the blanket.

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Figures captions

Fig.1 The amount of retained deuterium owing ion implantation only (Q) and absorbed deuterium gas (q) at temperatures of 380 K (a) and 773 K (b) as a function of deuterium ion fluence and gas fluence.

Fig.2 Change of hydrogen gas pressure in an absorption chamber during heating from 473 to 873 K.

Fig.3 SEM photographs of the irradiated samples with the fluence of 5×10^{21} He/m² (=45 dpa) (a), after heating up to 673 K in vacuum (b) and after heating at 1473 K (c).

Fig.4 Thermal desorption spectra of helium of the V-4Cr-4Ti alloy samples irradiated at room temperature..

Fig.5 The total amount of retained helium and those corresponding to Peak I, II and III in the V-alloy sample as a function of the helium ion fluence.

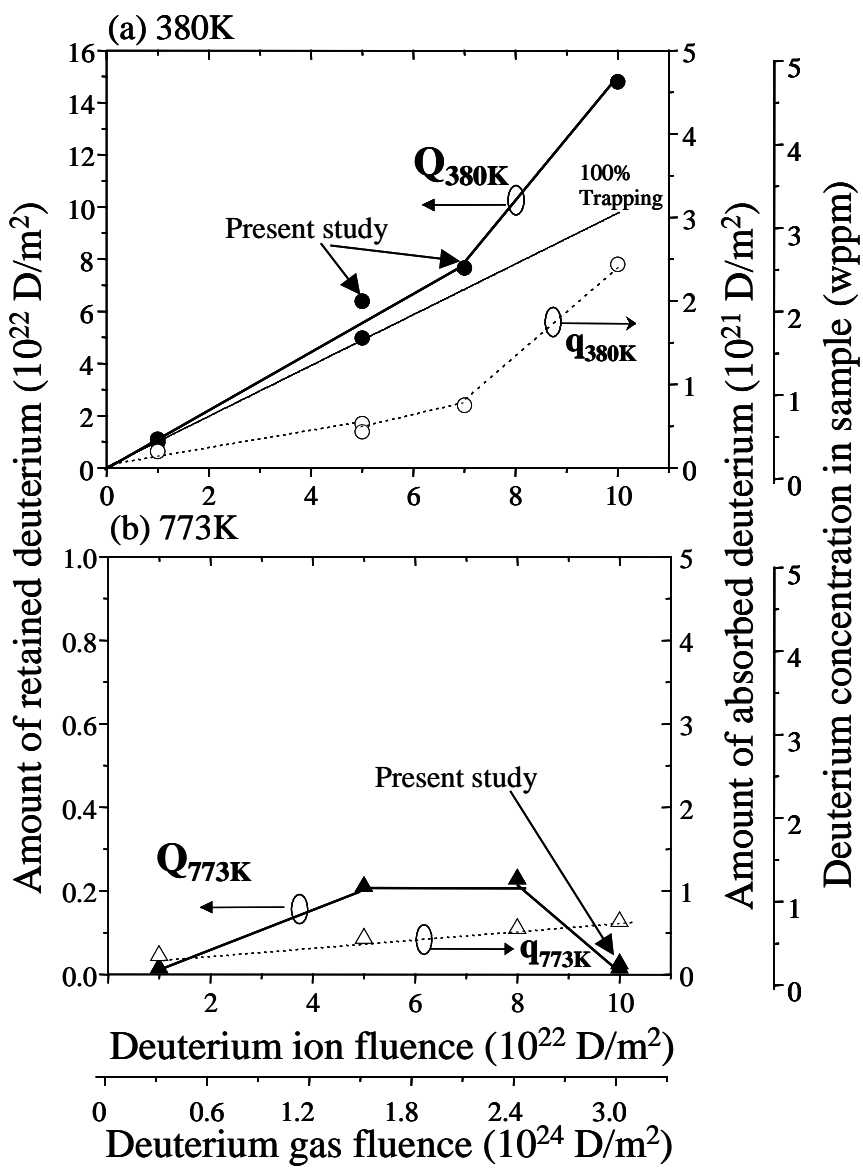


Fig.1 Hirohata

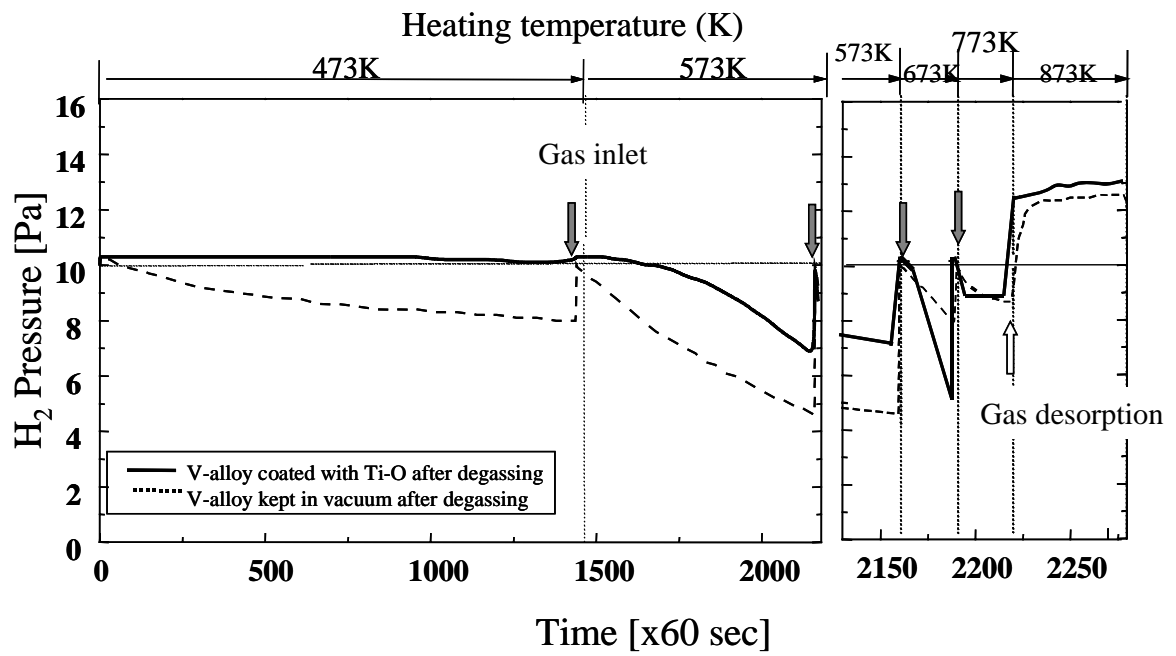
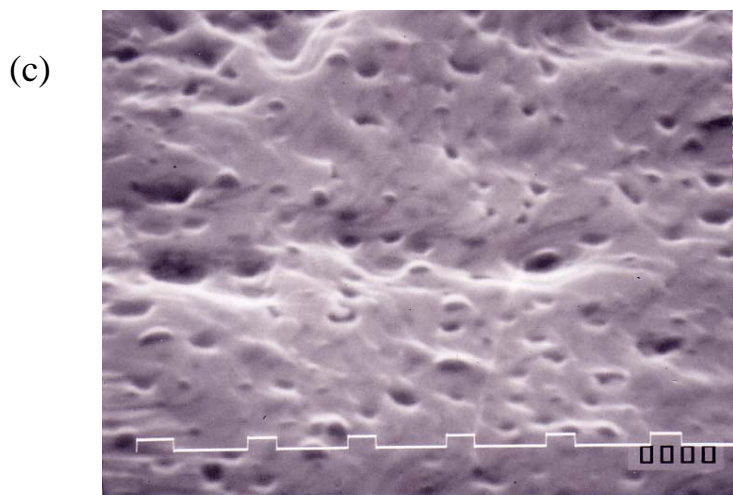
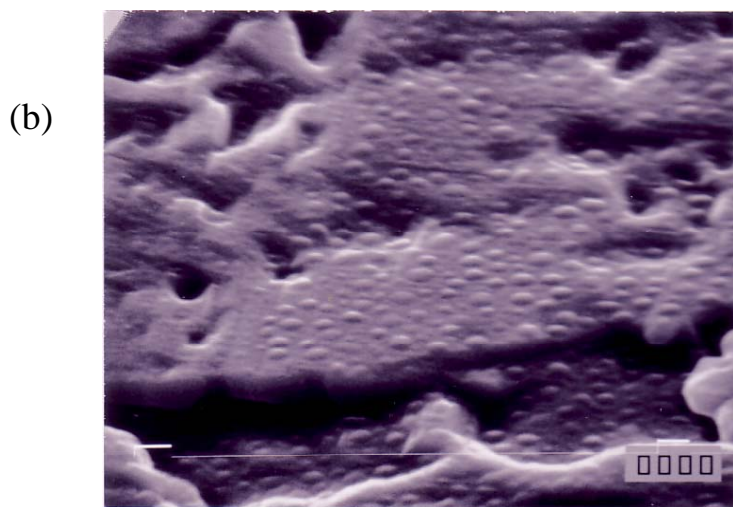
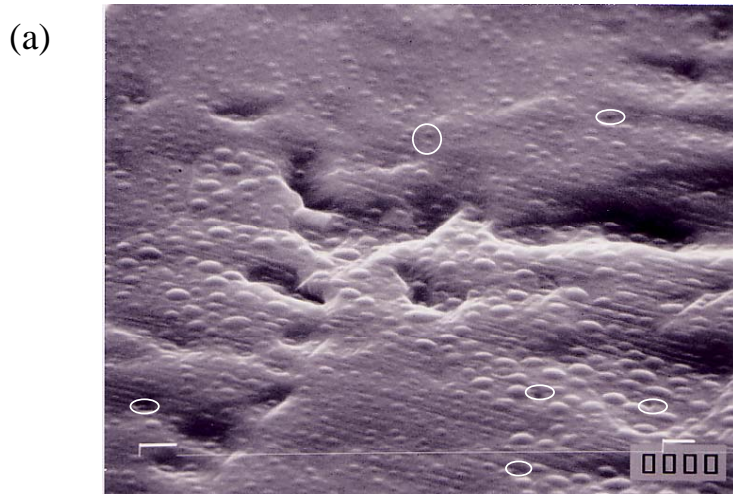


Fig.2 Hirohata



1 μ m

Fig.3 Hirohata

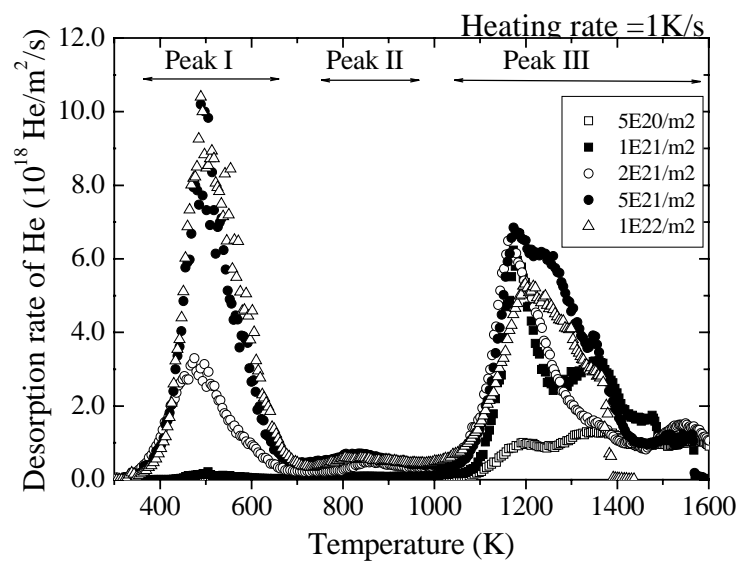


Fig.4 Hirohata

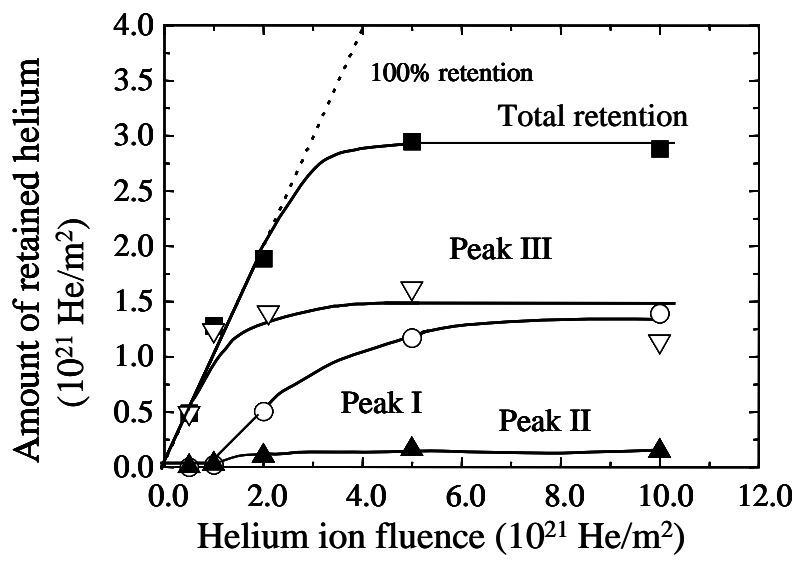


Fig.5 Hirohata