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Hydrogen micro-kinetics in titanium under mechanical stress studied by ion beam analysis ☆

T.S. Wang [a,*], H.Y. Lv [a], D. Grambole [b], Z. Yang [a], H.B. Peng [a], Y.C. Han [a]

[a] School of Nuclear Science and Technology, Lanzhou University, Lanzhou 730000, China
[b] Forschunszentrum Dresden-Rossendorf, Dresden, D-01314, Germany

A B S T R A C T

Hydrogen (H) is continuously produced by the large dose fast neutron irradiation on fusion reactor material. The concentration, diffusion and evolution of H in the structure material may cause H-embrittlement. Ion beam analysis is one of the most useful methods for studying the micro-kinetics of H in solids. In this work, the H-distribution in titanium (Ti) has been studied by resonance nuclear reaction analysis (resonance-NRA) and micro-elastic recoil detection analysis (micro-ERDA). The evolution of H-depth-profile in titanium samples has been studied versus the change of normal stress. Evident H diffusion has been observed, while a normal stress is changed in the range of 107–963 MPa. The H diffusion is related to the concentration of H in samples.

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1. Introduction

Hydrogen can be continuously produced by fast neutron irradiation on fusion reactor material through the (n,p) nuclear reaction and also the H-plasma implantation in the first wall. The concentration, diffusion and evolution of H in the structure material may cause serious change of material properties, e.g. H-embrittlement. In order to understand the micro-kinetics of H in material, various analysis methods have been applied. Ion beam analysis (IBA) method is one of the most efficiently methods to study the H behaviours in nano- or micrometer resolution [1–4]. In this work, the H-depth-profile in titanium (Ti) has been studied by resonance nuclear reaction analysis (resonance-NRA) and micro-elastic recoil detection analysis (micro-ERDA). The micro-ERDA offers the analysis of H-lateral distribution in micrometer scale [4,5], and the NRA with the ^{1}H (^{15}N, $\alpha\gamma$) ^{12}C resonant reaction provides the possibility to study the H-depth distribution in nano-scale [1,2,4]. Combining both methods, a three-dimensional distribution of H in titanium can be obtained in most of the solids. The micro-kinetics of H in Ti has not been well understood due to the limited H-analysis methods in micrometer scales. The evolution of H-depth-profile in a titanium sample has been studied versus the change of normal stress between 107 and 963 MPa.

2. Experimental

2.1. Analysis methods

The ion beam analyses were performed on the 3 MV tandetron and 5 MV tandem accelerators at the Forschungszentrum Dresden-Rossendorf [1,2,4].

H-depth-profiles with a depth-resolution up to 2 nm in samples were obtained by NRA with the ^{1}H (^{15}N, $\alpha\gamma$) ^{12}C resonant reaction, which has a resonant peak at 6385 keV with a width of 1.2 keV [2,3]. The gamma rays were detected by a BGO ($Bi_4Ge_3O_{12}$) detector behind the target in forward direction. $^{15}N^{+}$ ions with energies higher than 6835 keV reach the resonant energy in a certain depth due to the atomic stopping inside of the samples. Since the reaction cross section at resonant energy is about five orders of magnitude higher than the cross sections at other energies and the stopping power is nearly constant in this energy region between 5 and 12 MeV, thus, the gamma ray yield obtained at a certain projectile-energy corresponds directly to the H-concentration in the effective layer in a certain depth. The $^{15}N^{+}$ energy could be adjusted very slightly and continuously with the magnetic analyser at the tandem accelerator. A H-contamination may always be found on a silicon (Si) surface, so a Si-sample was used in this work to calibrate the $^{15}N^{+}$ energy, since maximum of the H-distribution on Si-surface corresponds to the resonant energy of 6385 keV. The depth was calculated by the energy difference dividing the stopping power, which is obtained from the SRIM code [6].

A three-dimensional H-distribution may be obtained by micro-ERDA with scanning of the nuclear micro-probe combined with the resonant NRA [2,3]. 15 MeV Si^{5+} ions were used as incident

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* Corresponding author.
E-mail address: tswang@lzu.edu.cn (T.S. Wang).

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projectiles in micro-ERDA. The ion beam was focused into a size of about 2 μm in diameter during a measuring time of several hours. The incident angle α was 70° to the normal of the specimens' surface. The recoiled H was detected by a surface barrier detector with a solid angle of Ω = 3 msr at a scattering angle of δ = 30° to the incident ion beam direction. A 10 μm thick aluminium foil was set in front of the detector to suppress the elastic scattered Si^{5+} ions from the sample surface. During the experiment, the ion beam was regularly switched into a Faraday cup placed before the micro-probe lens to monitor and normalize the measurements at each pixel. A lateral resolution of 10 μm(X) × 3 μm(Y) could be obtained. The detected data at each scan pixel were stored in list mode. In this way the H-loss during the measurement could be checked, too.

2.2. Samples description

The Ti-samples used in this study are pure Ti (99.6%) in size of 30 mm × 8 mm × 0.5 mm. The samples were mechanically polished at first, and then implanted with 25 keV/amu H_2^+ ions under a liquid-nitrogen cooling. In order to investigate the dose-dependence of the H-distribution, samples were implanted with 1×10^{17}, 3×10^{17} and 6×10^{17} H/cm^2, respectively. After the implantation the samples were stored in air at room temperature.

3. Results and discussion

3.1. The hydrogen diffusion under mechanical stress in titanium samples

An artifice normal stress was formed in the Ti samples by a convex bending (Fig. 1). The normal stress in samples could be calculated from the bending situation, they were 107, 321, 535, 749 and 963 MPa, respectively. The H-depth-profile in each bending situation was measured by the NRA with $^{15}N^+$ beam in size of 5 mm × 5 mm.

Three samples were analyzed at the sample stress situation in each run. An implanted H-peak can be found in the profiles at about 196 nm, which is just the implanted rang of the 25 keV/amu H_2^+ ions. In the sample implanted with a dose of 1×10^{17} H/cm^2, the H-concentration was below the analysis limitation. Thus the change of H-depth-profile with bending in the sample implanted with a dose of 3×10^{17} H/cm^2 is shown in Fig. 2.

In Fig. 2, the maximum H-concentration decreases, while the stress changes from 107 MPa to 936 MPa. It implies that the H diffuses to the place with less stress. However, in the sample implanted with a dose of 6×10^{17} H/cm^2, the depth-profile changes rather gradually, with the change of normal stress.

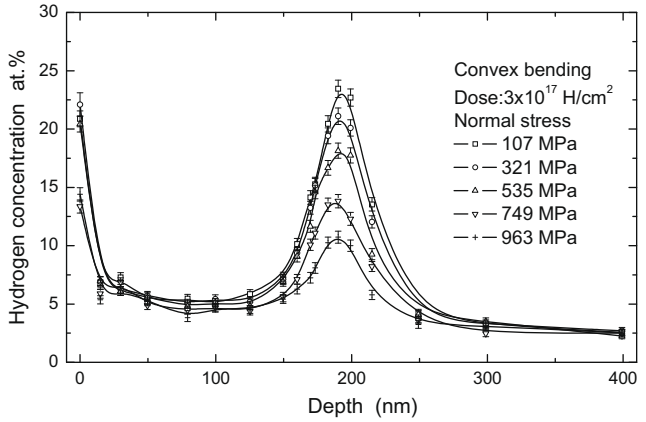

Fig. 2. H-depth-profiles versus normal stress in the Ti sample implanted with 3×10^{17} H/cm^2.

The relative ratio of H-concentration to that without stress in samples is used to descript the change of the H-concentration versus the normal stress in Fig. 3.

It is clear seen, the mobility of H in three samples was significantly different. The stability of H in sample increases with implantation dose, thus, the diffusion coefficient in samples is related to the implantation dose or H-concentration.

As we know, there are more than six different Ti/H phases, each phase has its own physical property and stability [2,4,5,7–9]. Therefore, the difference of diffusion coefficient in samples is due to the various chemical or physical states of H-atoms in samples. In the sample implanted with a dose of 1×10^{17} H/cm^2, the H-atoms were in solid solution situation (alpha-phase) in titanium. The atoms are in quasi-free state, thus, the H-atom may diffuse easily under stress. However, when the sample was implanted with the dose of 3×10^{17} H/cm^2, the gamma-phase of titanium hydride was formed, which is a semi-stable phase, the H-atoms are at bound state, but the chemical bound is easily broken under the mechanical stress. In the sample implanted with a dose of 6×10^{17} H/cm^2, a stable TiH_x phase (Delta-phase) was formed and the H-atoms were in bound state and could not diffuse freely [2,4,9].

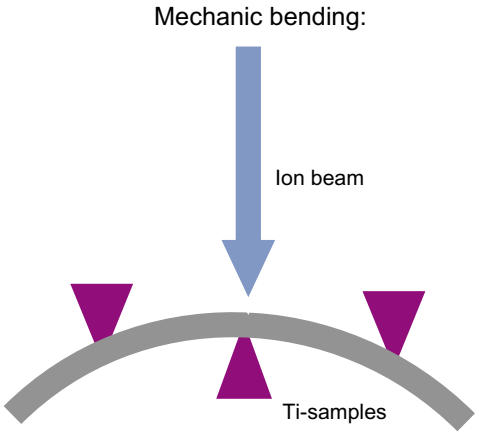

Fig. 1. Schematics of the convex bending and incident ion beam.

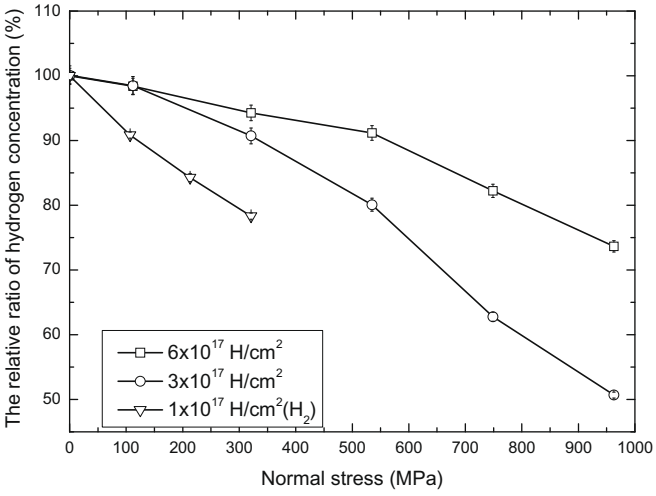

Fig. 3. The relative H-concentration versus normal stress in all samples.

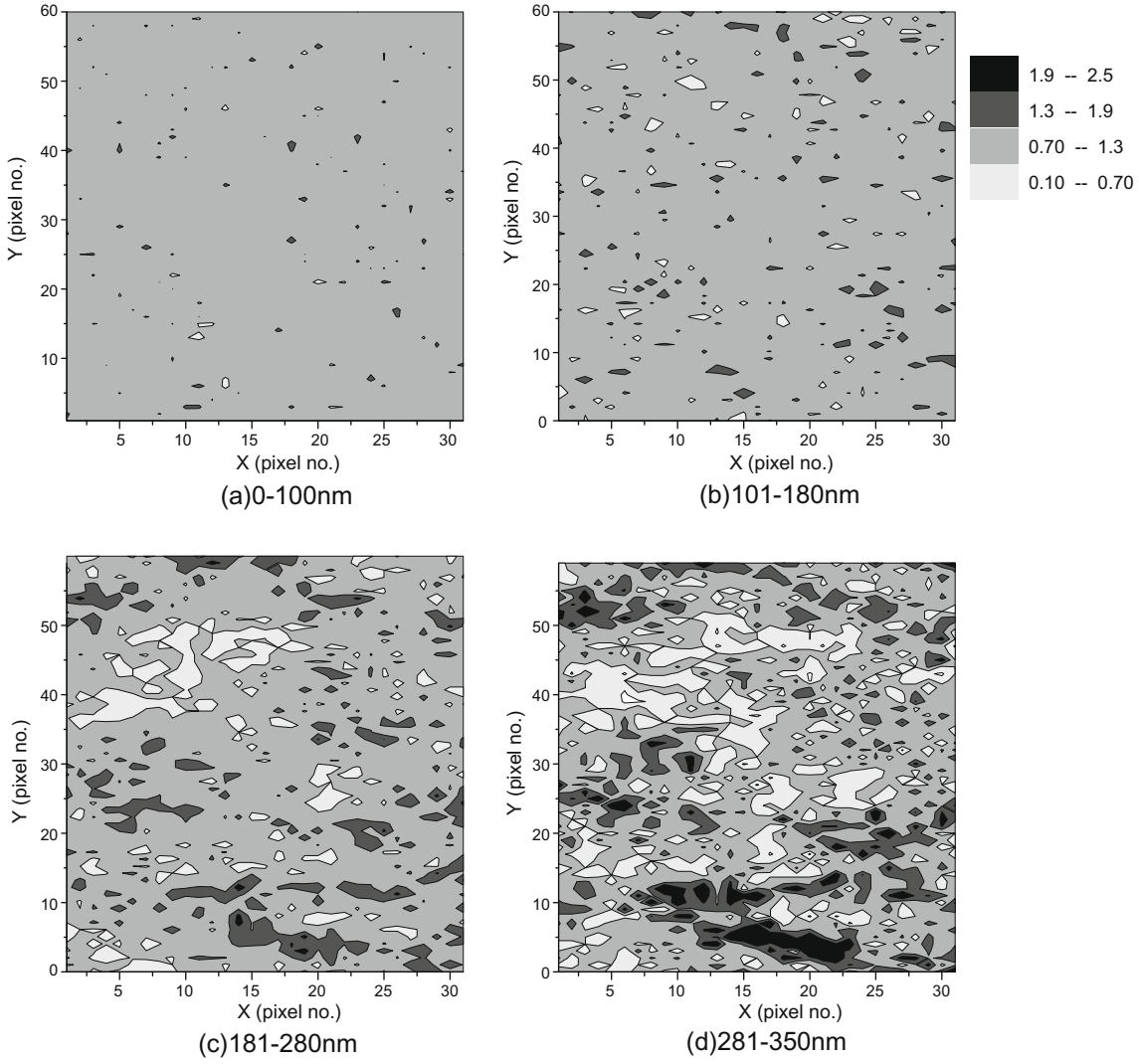

Fig. 4. Two-dimensional H-distribution maps in different depth regions in titanium.

3.2. The hydrogen lateral distribution measured in Ti/H sample

The three-dimensional distribution of H in a polished titanium sample implanted with a fluence of 6×10^{17} H/cm^2 was measured by scanning-micro-ERDA. The ion beam size was 3 μm. Mapping have been carried out by a scanning of $33(X) \times 60(Y)$ pixels, the corresponding area is 200 μm × 200 μm. The elastic recoiled proton spectrum is divided into four sections which represent different depth regions: 0–100 nm (a), 101–180 nm (b), 181–280 nm (c) and 281–350 nm (d). The maps of H-distribution in four layers are shown in Fig. 4.

The inhomogeneous H-distribution is observed in all four maps. In the layer (a) 0–100 nm, the H-distribution is almost homogeneous, but in the layer (d) 280–400 nm, the inhomogeneity of H-distribution is rather larger. Since the mobility of H in titanium is strongly related to the H-concentration [2,4,5,7]. The inhomogeneity is therefore also strongly H-concentration related. The re-distribution of H-concentration in Ti has been studied in previous work [7].

4. Conclusion

Ion beam analysis is a very powerful analysis method for H-analysis in nano- and micro-scale. H-depth-profiles in nano-meter resolution in Ti samples have been obtained by the NRA with the ^{1}H(^{15}N, $\alpha\gamma$)^{12}C resonant reaction. The diffusion of H-atom in Ti-samples under a mechanic bending was observed. The diffusion coefficient is related to the H-concentration. The higher is the H-concentration, the more stable are the H-atoms in Ti. A lateral scan micro-ERDA has been used for studying the H-lateral distribution in different depth layer. The inhomogeneity of H-distribution is various in different depth layers. It could be also another proof of that the mobility of hydrogen atom is related to H-concentration.

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