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Microprotrusions evolving from palladium subsurface deuterium-implanted at a cryogenic temperature

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ABSTRACT

Microscopic protrusions are shown to emerge from the Pd subsurface D-ion implanted at liquid-nitrogen temperature. Cross-sectional transmission electron microscopy has revealed that the protrusions were amorphous, suggesting that they were in a molten state during D-ion implantation. The amorphous area of the protrusion was commonly covered with a crystalline shell, the lattice of which expanded from the pure Pd lattice by around 5% that is in an agreement with previous works. The shell might have been of a deuteride structure stable in low-pressure ambiences.

1. Introduction

In relation to hydrogen fuel cells to be mass-produced in the close future, hydrogen-storage materials are now a global concern. One of such materials is palladium (Pd), which stores hydrogen gas up to 10^3 times its own volume at around room temperature. The reason of storage of H in Pd is that H cannot be easily desorbed into the environment at room temperature due to the high surface barrier and H is strongly trapped in Pd by a formation of hydride [1–2]. In a high-pressure gas-phase charge, occluded hydrogen (or deuterium) atoms rest at the octahedral sites, resulting in the formation of β-phase hydride (deuteride) with a hydrogen-Pd ratio of 0.706 for Pd-H and 0.658 for Pd-D [1,3]. These interstitial hydrogen atoms expand the original Pd lattice up to 5% [1]. When warming the mother crystal and/or reducing the ambient pressure, the interstitial hydrogen atoms diffuse out from the crystal, thereby increasing the hydrogen (deuterium) pressure in the ambient space. This is why Pd has been seen as a promising hydrogen-storage material.

In the H-occlusion mechanism stated above, incident H-atoms diffuse into the Pd lattice, so the hydrogen concentration monotonously decreases toward the interior until saturation is attained. When a Pd crystal is struck by energetic hydrogen (deuteron) atoms, by contrast, the projectiles are implanted in the subsurface where their concentration is maximized [4].

According to our investigations in the past fifteen years beginning from 1996 [5–7], low-keV hydrogen (H) or deuterium (D) ions striking a polycrystalline target of Pd at a high dose induce an anomalous event; viscous molten matter, like volcanic magma, flows out from the subsurface through surface craters (Fig. 1a). The chemical or physical process underling this phenomenon has remained to be elucidated, yet it is certain that, due to an oversaturation with hydrogen (deuterium), the crystalline subsurface transformed itself into a molten state.

The above molten matter was of an amorphous structure, within which Pd particles with nanometric dimensions were colloidally dispersed (Fig. 1b). The molten matter has thus been termed as the "matrix," of course tentatively [5]. (The substrate temperature, at which the matrix started to outflow, was about one-third of the melting point (T_m) of Pd (1550 °C At such an elevated temperature, the motion of hydrogen (deuterium) in Pd would be of long range, which may make it difficult to understand the nature of matrix outflow. If the target is at a cryogenic temperature, the rate of diffusion of hydrogen would be suppressed to nearly zero; implanted hydrogen atoms would be "trapped" in the Pd lattice. Indeed, Myers et al. have claimed that the [D]/[Pd] ratio at the subsurface D-ion implanted below 100 K can amount to 1.6 [6]. If so, how does such a super-, or hyper- [7], stoichiometry affect the structure of the subsurface? The original aim of the present study was to address this issue. Just recently, we noticed a close similarity of our work with the so-called "deuterium trapping" (DT) [8] in refractory metal lattice. This, too, stimulated this work.

2. Experimental methods

As in our previous experiments [9,10], the upper edge of a polycrystalline Pd platelet (99.99% in purity) polished chemically was

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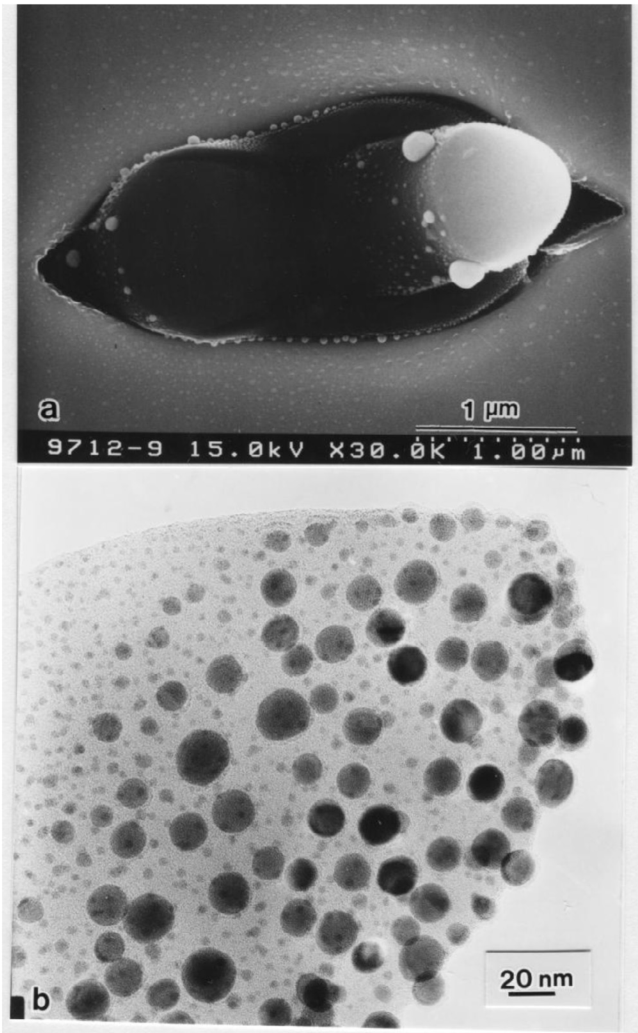
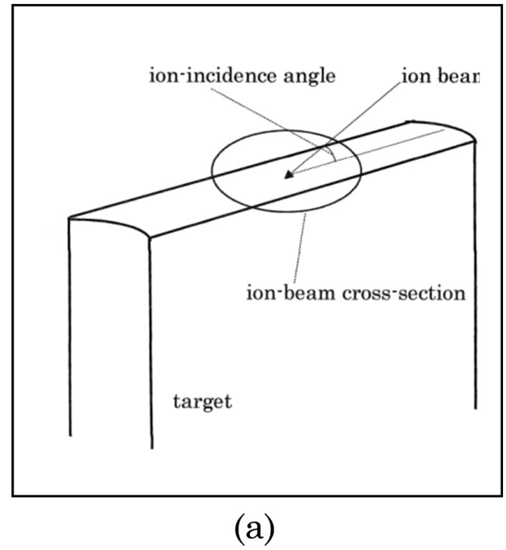


Fig. 1. (a) A matrix on a Pd target kept at ~400 °C (SEM image). (b) Matrix structure revealed by TEM.



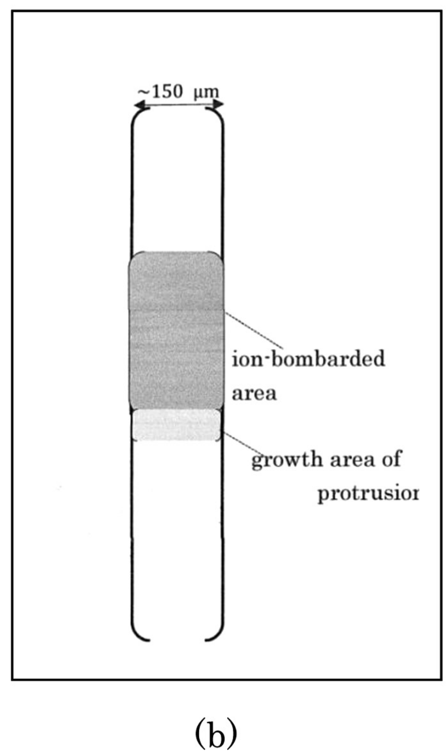


Fig. 2. (a) Ion incidence on target, shown schematically. (b) Top view of target after ion-bombardment (schematic).

bombarded with D-ions accelerated to 3 keV in a vacuum chamber linked to an Auger analyzer (Fig. 2(a)). The ion beam was focused into a microbeam ~300 μm in diameter, and the ion current density was regulated to $\sim 1 \times 10^3$ μA/cm^2, making for a dose rate of $\sim 5 \times 10^{17}$ ions/cm^2.min. The ions struck the sample at an oblique angle of 35°. Prior to D-bombardment, the sample surface was sputter-cleaned at room temperature, using 3 keV Ar^+ ions. The average crystalline size of the as-received sample was ~160 nm, as estimated by powder X-ray diffraction [11].

With the aid of the sample-cooling system installed in the chamber, the D-ion implantation was done at −185 °C, or liquid nitrogen temperature, during which little fluctuation was discerned in target temperature.

After D-implantation, the sample was transferred in air to an HS-5000 field emission (FE) scanning electron microscope (SEM), in order to observe surface morphology.

3. Results and discussion

FE-SEM observations disclosed microscopic protrusions distributed sparsely on the sample surface. Typical of such examples are shown in Fig. 3, which reveals protrusions emerging from the subsurface through a crater. As confirmed with a stereo-microscope, these protrusions grew just outside the ion-bombarded area (see Fig. 2(b)). If such protrusions were the "matrix," their inner structure must have been amorphous; the ion-implanted subsurface and its periphery, presumably supersaturated with deuterium, might have been in a molten-like state during ion implantation, regardless of sample cooling with liq. N_2.

To corroborate the above hypothesis, the structure of such protrusions must be determined by transmission electron microscopy (TEM). Unlike the matrix, however, the as-formed protrusions were not transparent to the TEM electron beams, so their thinning was indispensable to unveil their inner structure. We have already established a technique to make this possible [12,13], the basis of which is the focused-ion beam (FIB) technique [14].

The principle of FIB is to scan a focused Ga^+ ion beam extracted from a liquid-metal ion source over the pre-specified area of the sample. Since the Ga^+ ion beam is precisely positioned by