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# 2D mapping of hydrogen permeation from a stainless steel membrane

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ABSTRACT

Hydrogen permeation from a metal surface was visualized by two-dimensional mapping of hydrogen ion desorbed by scanning electron beam irradiation. The sample used was stainless steel containing dislocations of martensite; the sample was 100 μm thick, which is nearly the same as the grain size. One side of the sample was exposed to deuterium gas, and sites of deuterium permeation on the other side were visualized sequentially. There was a good correlation between the patterns of the permeation sites and the grain structure observed in secondary electron images.



The main component of the residual gas in a vacuum chamber under ultrahigh vacuum is hydrogen. The cause is attributed to release of hydrogen contained in the vessel material to the vacuum. Outgassing in vacuum systems has been reduced by new materials and surface treatments [1] such as surface polishing [2,3], titanium nitride coating [4], surface oxidation [5–7], and boron nitride coating [8]. We have reported that hexagonal boron nitride segregated onto stainless steel inhibits outgassing of hydrogen as measured by an electron-stimulated desorption (ESD) technique [8]. However, a better understanding of the process involved in the permeation of hydrogen from metal will likely lead to further progress in this field.

Metallic materials like stainless steel are used as structural materials in the construction of, for example, vacuum vessels and the main components of buildings, bridges, and aircraft that need to withstand severe conditions. The physical and mechanical properties of such structural materials are very important in order to ensure the integrity of these components and the safety of human life. Metal corrosion and hydrogen embrittlement deteriorate the mechanical properties of such materials, and atomic hydrogen diffusing in a metal and accumulating at critical sites causes growth of cracks, causing serious problems and leading to extremely dangerous phenomena.

Presently, it is difficult to say that the phenomenon of hydrogen permeation and embrittlement is fully understood. Hydrogen detection, in particular, seems to be one of the most difficult aspects of the problem. Hydrogen atoms within a diffusion channel and at trapping sites cannot be detected directly. In this study we focused on the diffusion of hydrogen in a duplex stainless steel and its permeation to the surface.

Depth profiling of hydrogen has been observed by nuclear reaction analysis [9]. However, it is difficult to directly catch the dynamical diffusion of hydrogen with real-time observations. Visualization of local hydrogen distributions on the surface has been attempted by several methods, including a hydrogen micro-print technique [10], secondary ion mass spectrometry [11], Kelvin probe force microscopy [12], and tritium autoradiography [13]. The ESD technique is a powerful investigative tool for surface analysis that utilizes electrons to stimulate excitation of the bonding state between adsorbed atoms and the surface. From here on, we refer to ESD as "desorption induced by electronic transitions (DIET)" in order to highlight the desorption mechanism involved in ESD. Ions desorbed by DIET contain a large amount of information relevant to the study of the bonding and dynamical behavior of species chemisorbed on a surface. In addition, the DIET technique has been shown to perform well in detecting the distribution of hydrogen on a surface [8,14,15]. Our current study is the first to apply a scanning electron beam to the visualization of permeated hydrogen. Our method makes real-time visualization possible. Also, because the sample temperature can be increased up to about 573 K, hydrogen permeation can be observed in a short time.

In a previous study, we reported the distribution of hydrogen seeping from the bulk of a sample (a stainless steel membrane) to the surface by DIET ion measurement [17]. The main ions desorbed by DIET originated from surface hydrogen, most of which was supplied from the backside of the sample membrane. Hydrogen adsorbed on

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the backside permeated to the opposite surface through solution into the bulk and diffusion within the bulk. The behavior of hydrogen on the inside of the metal was deduced from the DIET mapping of hydrogen ions on the sample surface, which was characterized by the intrinsic grain structure or by the machining process [8,16,17]. On the machined surface, the grain structure of the stainless steel could not be detected by scanning electron microscope (SEM). However, striped patterns made by machining with the lathe were observed on both secondary electron images and in the DIET ion mapping. The pattern of hydrogen revealed by DIET reflected the topographical pattern made by the lathe machining, and we reported that the density of the dislocations on the austenite stainless steel surface that occurred as a result of machining had an influence on surface hydrogen concentration [16]. Also, we have tried to determine the relationship between the grain structure of the sample and the surface hydrogen distribution. The stainless steel membrane was 100 μm thick and had an austenite structure including martensite dislocations; the size of the austenite grains (100–150 μm) is comparable to the thickness of the membrane. DIET ion images were observed at different temperatures, and we found that the sites where hydrogen was detected in high concentration at 373 K were different from the incremental sites at 523 K. We consider that the former increase was due to diffusion through the martensite phase and the latter was due to diffusion through the austenite phase [17].

In this paper, we report the real-time observation of hydrogen permeating to the surface. The DIET signals were measured in a two-dimensional pulse counting system constructed with a LabVIEW USB-6341 Multifunction I/O Device (National Instruments) and synchronized with the scanning electron beam. The collecting electrode is attached so as to cancel out the topological effects found in the DIET patterns.

The sample was stainless steel (SUS304) that included martensite dislocations in an austenite structure created by cold rolling with 20% reduction in thickness. The grain size (100–150 μm) was measured with an optical microscope. The austenite and martensite structures were confirmed by X-ray diffraction (RINT2500; Rigaku). The thickness of the sample was 100 μm, which was nearly the same as the grain size. The sample was prepared by the following process and mounted in the measurement positon. The center area (5 mm diameter) of a circular plate (SUS304, including the martensite dislocations) of 1 mm thickness was thinned to 100 μm with a milling machine. The plate was then welded to ICF34 flange through a short pipe. The temperature of the center area was kept below 373 K to avoid structural modification by the heat of welding.

Fig. 1 shows a schematic diagram of the experimental setup. The hydrogen reservoir with the sample, DIET ion detection system, and the quadrupole mass analyzer (QMG220; Pfeiffer) are incorporated with the sample chamber of a commercially available SEM (JAMP10; JEOL). The reservoir is connected to an independent pumping system and a cylinder of hydrogen. The focusing electrode is set near the sample in order to focus DIET ions to the entrance of the detection system. Base pressure of the sample chamber was set to $1.0 \times 10$–7 Pa with an ion pump (PUT-3;ULVAC) and the reservoir pressure was set to $6.0 \times 10$–4 Pa with a turbo molecular pump (HiPace 80; Pfeiffer). Deuterium gas was supplied at 0.25 MPa during experiments. The sample temperature was controlled from room temperature (RT = 290 K) up to 573 K by heating with a halogen lamp (10.8 V, 30 W; Toshiba). The temperature was increased by about 0.01 K/s to the setting temperature (573 K). The temperatures were monitored by a type-T thermocouple directly connected to the sample plate.

ESD is usually used in studies of adsorption. An adsorbed atom is excited to an antibonding state by electron irradiation, and is desorbed as

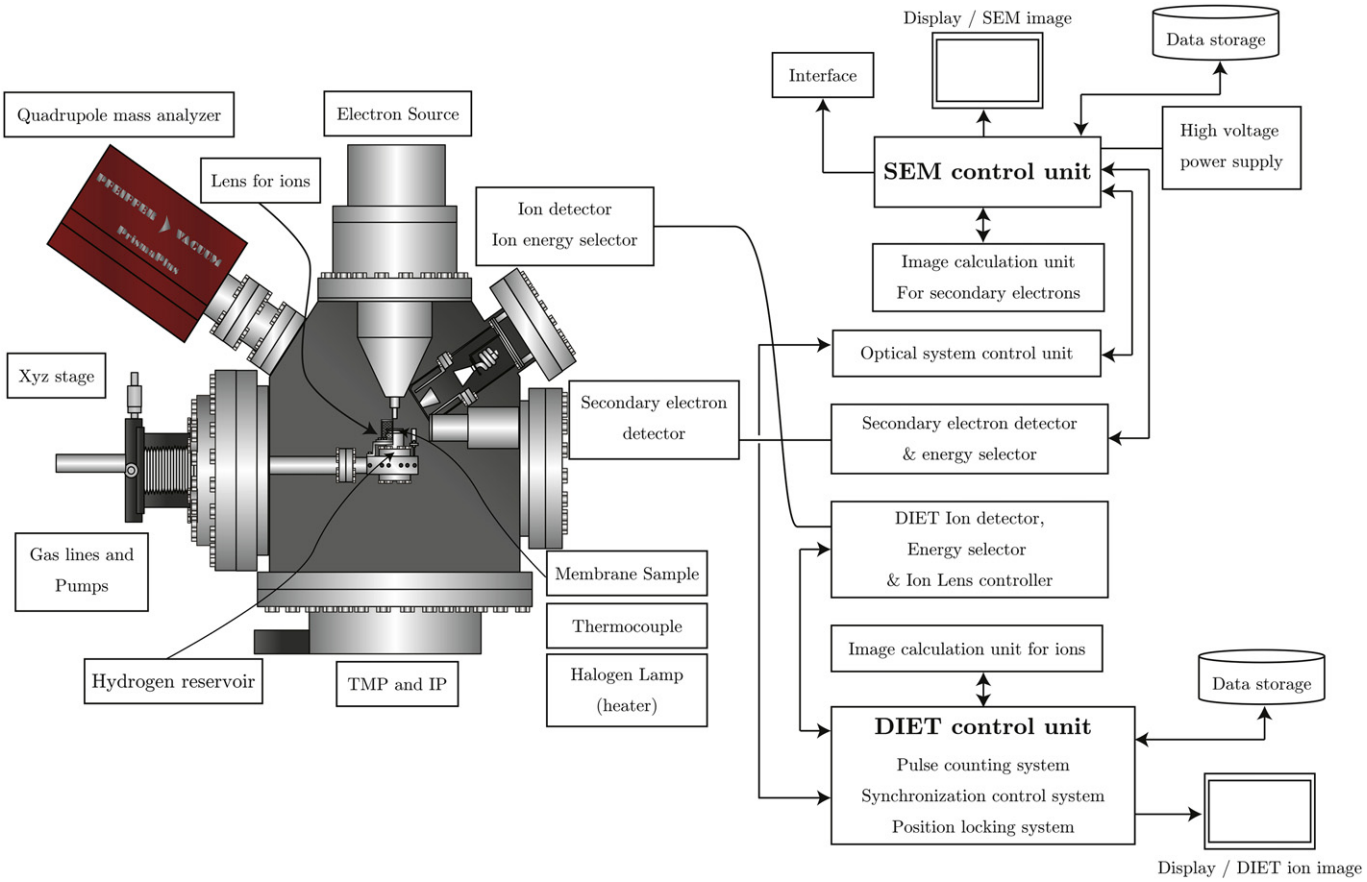


**Fig. 1.** Experimental setup.