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Temperature dependence of hydrogen depth distribution in the near-surface region of stainless steel

Kotaro Takeyasu [a, *], Masuaki Matsumoto [b], Katsuyuki Fukutani [a]

[a] Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan
[b] Department of Physics, Tokyo Gakugei University, 4-4-1 Nukuikitamachi, Koganei-shi, Tokyo 184-8501, Japan

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ABSTRACT

The depth profile of hydrogen at a type 304 stainless steel surface was investigated with $^{1}H(^{15}N, \alpha\gamma)^{12}C$ nuclear reaction analysis at various temperatures. Hydrogen was predominantly distributed in the region shallower than 10 nm (surface hydrogen) with an area density of ~1×10^{16} cm^{-2}. Hydrogen was found to also exist in a deeper region (>30 nm) with a constant volume density of ~4×10^{20} cm^{-3} (bulk hydrogen). While both bulk and surface components gradually decreased as the temperature rose, part of the intensities remained even at 975 K. From the temperature dependence of the amount of the surface hydrogen, the distribution of the activation energy for desorption is discussed.

1. Introduction

Water and molecular hydrogen are most abundant residual gases in unbaked and baked vacuum systems made of stainless steel, respectively. In the case of water, the adsorption energy has been shown to reveal a distribution [1–4], which means that water exists in various adsorption states. The adsorption type is considered to include dissociative adsorption, coordinative adsorption, adsorption through hydrogen bond and formation of hydroxides [5].

Residual hydrogen is, on the other hand, considered to be derived from hydrogen atoms in the bulk and on the surface. The bulk hydrogen atom diffuses and reaches the surface. Then, as well as surface-adsorbed hydrogen, the bulk-derived hydrogen atoms are recombined and desorbed as hydrogen molecules [6]. This indicates that the binding energy and depth distribution of hydrogen species near the surface directly influence the outgassing rate of water and hydrogen in a vacuum system.

Only a few works have studied the depth profile of hydrogen in stainless steel [7–9] because of the experimental difficulty to quantitatively detect hydrogen. Nuclear reaction analysis (NRA) studies with H-specific $^{1}H(^{15}N, \alpha\gamma)^{12}C$ showed that stainless steel contains hydrogen of ~5×10^{16} cm^{-2} at the surface and 10^{20}–10^{21} cm^{-3} in the bulk [7,8]. Furthermore, a study with position-sensitive atom probe (PoSAP) suggested that deuterium coexists with Cr, Ni, and O rather than Fe in stainless steel, and the existence of strongly bound hydrogen in nickel hydride and nickel hydroxide was proposed [9]. However, the thermal stability of hydrogen at each depth, which directly influences the outgassing in a vacuum remained to be done.

In the present paper, the temperature dependence of the hydrogen depth profile for a type 304 stainless steel was studied with NRA. The distribution of the activation energy for hydrogen desorption was analyzed on the basis of the experimental data, which is discussed to show a wide distribution from 1.1 to 2.4 eV.

2. Experimental

The sample used in this study was a type 304 stainless steel piece with a size of 12 × 12 × 1.5 mm^3. Its bulk composition confirmed by X-ray fluorescence analysis was Fe:71.6, Cr:18.6, Ni:8.4, Mn:1.0, Cu:0.1, V:0.1, and Mo:0.1 in mol%. The sample was rinsed with an ultrasonic cleaner in acetone, ethanol and distillated water without particular surface treatments.

The hydrogen depth profile was quantitatively investigated by the H-specific $^{1}H(^{15}N, \alpha\gamma)^{12}C$ nuclear reaction at the 1C beamline of the 5 MV Van de Graaff Tandem accelerator in the Microanalysis Laboratory (MALT) of The University of Tokyo [10]. The typical base pressure in the measurement chamber was 1×10^{-5} Pa. The $^{15}N^{2+}$ ion beam irradiated the sample surface at a current of 40–100 nA

* Corresponding author.
E-mail addresses: takeyasu@iis.u-tokyo.ac.jp (K. Takeyasu), fukutani@iis.u-tokyo.ac.jp (K. Fukutani).

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and a beam diameter of 2–4 mm on the surface at room temperature. The 4.43 MeV γ-ray emitted in the nuclear reaction provides the signal proportional to the H concentration. H depth profiles were obtained by recording the γ-ray yield as a function of the incident $^{15}N^{2+}$ ion energy (E_i). Since the nuclear reaction is resonanced at the resonance energy (E_{res}) of 6.385 MeV with a width of 1.8 keV, E_i and the stopping power (dE/dz) (3.61 keV/nm for type 304 stainless steel) [11] define the probing depth (z) as $z = (E_i - E_{res})/(dE/dz)$. The depth resolution is mainly limited by the width of the Doppler-broadened energy resonance peak at $E_i = E_{res}$, which typically amounts to a few nanometers [12]. The γ-ray yield is quantitatively replaced with the H density by calibration of the γ-detection efficiency with a sample of known H concentration, in our case a kapton film. The typical measurement time of a profile was 40 min.

3. Results

Fig. 1(a) shows NRA profiles for a type 304 stainless steel surface heated to temperatures of 300–975 K. The NRA profile was taken with the sample kept at respective temperatures except that at 975 K. After a measurement, the temperature was raised to the next temperature in an incremental manner. The heating time was therefore in accordance with the measurement time of NRA, which is about 40 min. The sample was finally heated at 975 K for 5 min, and the NRA profile was taken after the temperature was decreased to room temperature. The profile for the 300 K sample reveals a maximum at E_i of 6.388 MeV, which is 3 keV higher than the resonance energy. The peak has a FWHM of 17 keV and a tailing feature at a high-energy region. This firstly indicates that the near-surface region with a thickness of ~10 nm contained a substantial amount of hydrogen (surface hydrogen). This probably corresponds to hydrogen in a metal oxide layer. Secondly, the bulk region (E_i > ~6.50 MeV) also contained a certain amount of hydrogen (bulk hydrogen). Both surface and bulk components were reduced in intensity by the increase of the temperature, however, they remained even after annealing at 975 K.

Fig. 1(b) shows the average γ-ray yield in the bulk region as a function of temperature. The right axis in Fig. 1(b) denotes the volume density of the bulk hydrogen calculated from the γ-ray yields. It is apparent that the volume density of the bulk hydrogen immediately start to decrease by elevating the sample temperature and remains almost constant above 550 K. The result implies that there are at least two types of hydrogen in this depth region: One is removed by heating up to 550 K and the other remains above 550 K. Fe, Cr and Ni can contain hydrogen as solid solution with different enthalpies [13]. Furthermore, Ni forms hydride with an enthalpy of −0.30 eV/atom [13]. The different thermal stability of the bulk hydrogen is considered to reflect the differences in the binding state of hydrogen in the sample.

Fig. 1(c) shows the integral of the γ-ray yield for the surface hydrogen from which the average γ-ray yields of the bulk hydrogen are subtracted. The average γ-ray yield for 450 K is assumed to have the average value between the value for 400 K and 550 K. The integral corresponds to the area density of the surface hydrogen, which is plotted on the right axis in Fig. 1(c). The area density of the surface hydrogen was 1.3×10^{16} cm^{-2} at 300 K. Then it gradually decreases above 400 K and remains constant even at 975 K.

4. Discussion

The thermal stability of the surface hydrogen is discussed in this section. It is assumed that their thermal stability in the oxide layer reflects the effective activation energy for desorption E_d of the entire outgassing process of hydrogen.

In a metal oxide layer, possible adsorption states of hydrogen that desorbs at above 300 K include H at an interstitial site (H_{int}), H bound to a metal atom (H–M) and an oxygen atom (H–O), and chemisorbed H_2O [14]. The rate-determining step for the release is considered to be desorption from the surface [15,16]. Up to 400 K, as

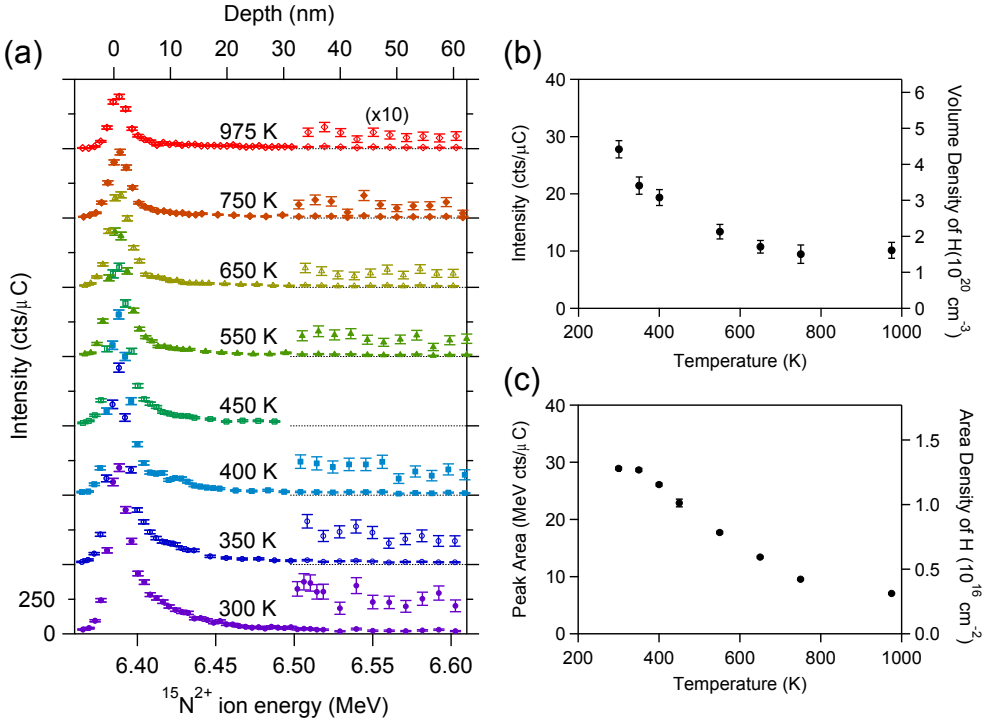

Fig. 1. (a) NRA profiles on a type 304 stainless steel surface measured at different temperatures. (b) γ-ray yields averaged over 6.50–6.60 MeV. (c) The integral of the surface component of the NRA profiles, which was obtained by subtracting the bulk value from the total yield of the profiles.