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Highly sensitive secondary ion mass spectrometric analysis of time variation of hydrogen spatial distribution in austenitic stainless steel at room temperature in vacuum

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ABSTRACT

Hydrogen contained in austenitic stainless steel is classified as diffusible or nondiffusible. The hydrogen distribution in austenitic stainless steel changes with time owing to hydrogen diffusion at room temperature, and such changes in hydrogen distribution cause the mechanical properties of the steel to change as well. It is therefore important to analyze the time variation of the hydrogen distribution in austenitic stainless steel at room temperature to elucidate the effects of hydrogen on the steel's mechanical properties. In this study, we used secondary ion mass spectrometry (SIMS), a highly sensitive detection method, to analyze the time variation of the distribution of hydrogen charged into 316L austenitic stainless steel. SIMS depth profiles of hydrogen that were acquired at the three measurement times were analyzed, and the results were compared among the measurement times. $^{1}H^{-}$ intensities and distribution of the intensities changed with time due to diffusion of hydrogen in the hydrogen-charged 316L steel sample at room temperature. Moreover, the time variation of the hydrogen concentration distribution of the hydrogen-charged 316L sample was calculated using a one-dimensional model based on Fick's second law. The time variations of the measured hydrogen intensities and of the calculated values are compared.

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1. Introduction

Austenitic stainless steel is a metallic material used for fuel-cell vehicles or hydrogen infrastructure. When the material is exposed to hydrogen gas, hydrogen atoms enter the material. The hydrogen atoms in the material can degrade its mechanical properties by means of "hydrogen embrittlement," a phenomenon that has been studied extensively [1–7,22–28].

Murakami et al. analyzed hydrogen contained in a hydrogen-charged 316L austenitic stainless steel using thermal desorption spectroscopy (TDS), and revealed that the hydrogen-charged stainless steel contained both diffusible and nondiffusible hydrogen [3]. Nondiffusible hydrogen is hydrogen that enters the steel at the time of manufacture, and is present even in uncharged (with no hydrogen charging) 316L austenitic stainless steel, with very little diffusion at room temperature. When uncharged 316L stainless steel is exposed to hydrogen gas, hydrogen entering the steel diffuses in the steel at room temperature, so that the concentration distribution of the diffusible hydrogen changes over time. Changes in the concentration distribution of the diffusible hydrogen are likely to cause changes in the mechanical properties of the 316L austenitic stainless steel [1–5,22–28]. It is therefore important to analyze the time variation of hydrogen distribution in 316L austenitic stainless steel to understand the effects of hydrogen on the steel's mechanical properties.

Recently, we have developed a highly sensitive detection method for hydrogen using secondary ion mass spectrometry (SIMS), and used this method to observe the distribution of hydrogen charged into 316L austenitic stainless steel [15]. When hydrogen in a sample is measured with SIMS, not only net hydrogen (H_N) in the sample but also background-originated hydrogen (H_{BG}) is simultaneously detected. The HBG originates from moisture (H_2O), hydrocarbons (C_xH_Y), or organic materials ($C_xH_YO_Z$) existing in the SIMS chamber or on the sample surface [8]. This H_{BG} precludes an accurate measurement of H_N because H_{BG} and H_N cannot be distinguished in a SIMS profile. Carbon, oxygen, and nitrogen in residual gas in a SIMS chamber or on an inner surface of the chamber are also likely to be background sources when carbon, oxygen, and nitrogen contained in a sample are analyzed with SIMS. There have been several studies of background sources and effective methods to improve detection limits in SIMS analysis of hydrogen, carbon, oxygen, and nitrogen in semiconductor materials [9–14]. To accurately analyze hydrogen charged into 316L stainless steel samples, further improvements to these methods are needed because even uncharged 316L stainless steel contains hydrogen that enters the steel at the time of manufacture, and because the amount of H_{BG} emitted changes with time during SIMS measurements. However, in past studies, gross intensity of hydrogen (total intensity of H_N and H_{BG}) has been merely considered in SIMS analysis of hydrogen in metallic material [19–21]. The original highly sensitive detection method developed by the authors consists of a procedure in which a silicon wafer is sputtered by a SIMS primary ion beam near an analyzed area to reduce H_{BG} in SIMS measurement of hydrogen, and a method to determine the intensities of H_{BG} in measurements of a hydrogen-charged sample by estimating the time variation of hydrogen intensities in measurements of an uncharged sample [15]. In the present study, the time variation of the distribution of hydrogen charged into 316L austenitic stainless steel at room temperature in vacuum is revealed by our SIMS method. In addition, the time variation of the hydrogen concentration distribution in the hydrogen-charged 316L sample is calculated using a one-dimensional model on the basis of Fick's second law. The time variations of the measured hydrogen intensities and of the calculated values are compared.

2. Experimental procedure

2.1. *Samples [15]*

The 316L austenitic stainless steel (iron-base, 0.01 wt% C, 0.53 wt% Si, 0.77 wt% Mn, 0.023 wt% P, 0.001 wt% S, 12.13 wt% Ni, 17.16 wt% Cr, and 2.86 wt% Mo) was used for this study. Fig. 1(a) shows two rod-shaped samples manufactured from the 316L steel with a diameter of 5 mm and length of 40 mm. One sample (H-PRECHARGE-0) was treated by ultrasonic washing with acetone and then exposed to hydrogen gas at 10 MPa and 250 °C for 192 h with the hydrogen exposure facility HYDROGENIUS [17]. After hydrogen exposure, the bulk hydrogen concentration was 22.4 mass ppm. Another sample (NON-CHARGE-0) was prepared to estimate H_{BG} in SIMS measurements of H-

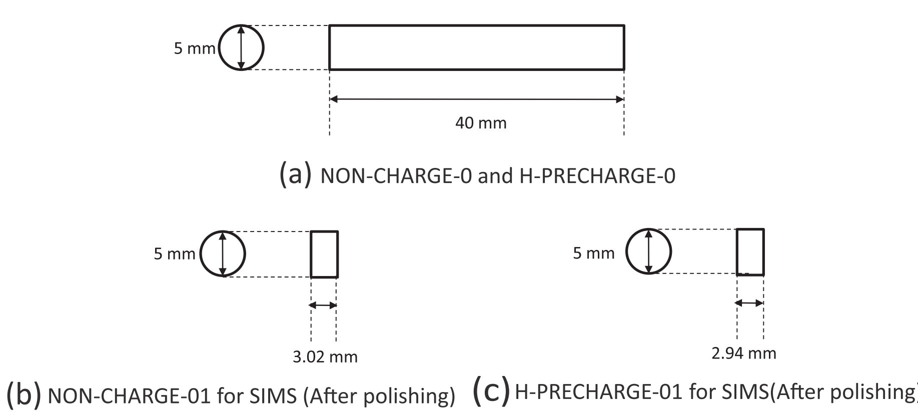

Fig. 1 – Dimensions of the 316L austenitic stainless steel samples [15].