

## Visualization of Hydrogen Permeation Through Stainless Membrane Using Electron Stimulated Desorption

Akiko N. Itakura<sup>1</sup>, Yoshiharu Murase<sup>2</sup>, Taro Yakabe<sup>1</sup>, Masahiro Kitajima<sup>1</sup>, Naoya Miyauchi<sup>3</sup> and Satoka Aoyagi<sup>4</sup>

<sup>1</sup>. Surface Physics and Characterization Group/National Institute for Materials Science, Ibaraki, Japan.

<sup>2</sup>. Corrosion Property Group/National Institute for Materials Science, Ibaraki, Japan.

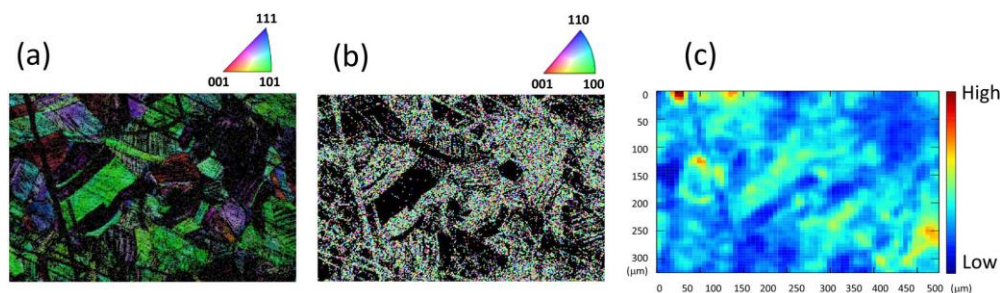
<sup>3</sup>. Materials Analysis Station//National Institute for Materials Science, Ibaraki, Japan.

<sup>4</sup>. Department of Material and Life Science/Seikei University, Tokyo, Japan

\* Corresponding author: itakura.akiko@nims.go.jp

One of the biggest issues in hydrogen economy is “hydrogen embrittlement” of metal induced by hydrogen entering and diffusing into materials. The dynamics of hydrogen in metals with mixed grain structure is not well understood at microscopic scale. Hydrogen diffusion in metallic materials is difficult to grasp owing to the non-uniform compositions and structures of metal. We have developed “operando hydrogen microscope” to visualize hydrogen by using ESD (electron stimulated desorption) method [1]. We succeeded into measuring the diffusion of hydrogen permeation quantitatively and locally with the operando hydrogen microscope [2,3]. We also visualized the hydrogen released from the metal material through the hydrogen diffusion barrier coated on the substrate material [4]. In this paper, we will introduce the observation of hydrogen permeating through the metal sample and the model of hydrogen diffusion using the results [5].

The sample was cold rolled stainless steel which had regions with locally different balance between austenite and martensite but with the same overall chemical composition. The structures were determined by EBSD (electron backscatter diffraction) measurement as shown in figure1 (a) and (b). Figure 1 (c) is the distribution of hydrogen permeating through the membrane sample thickness of 100  $\mu\text{m}$  at the same area with (a) and (b). The color bar indicates the hydrogen ion counts at each position. The ion counts were integrated over 65 hours (520 images) of permeating hydrogen from the time that hydrogen was first introduced to the bottom of the sample.

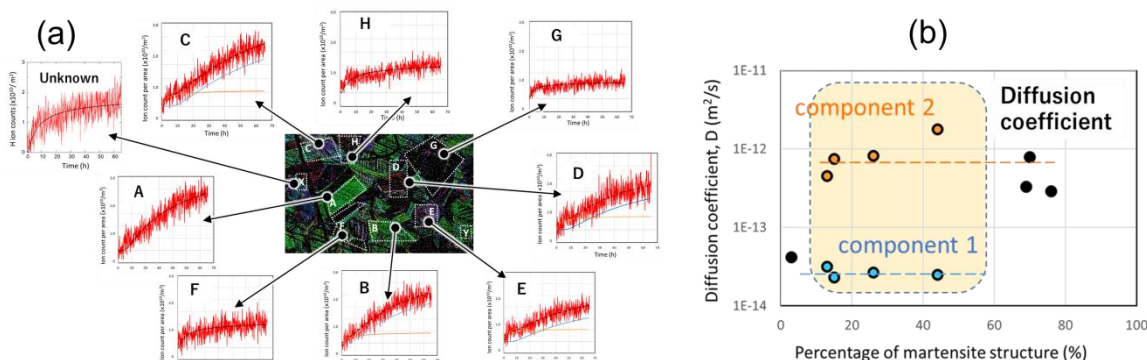


**Figure 1.** Sample structures and hydrogen map of the same area. (a) Inverse pole figure (IPF) map for austenite in a sample of cold-worked SUS304 stainless steel. (b) IPF map for martensite at the same position as (a). The colors in the IPF maps represent the crystal orientation when viewed from the normal direction (ND), shown in each upper right. (c) Distribution of hydrogen permeating through the sample. The color bar indicates the hydrogen ion counts integrated 65 h at each position.

We picked up regions A to H and X (shown in dotted frames IPF map in figure2 (a)) from which characteristics were extracted. The sizes of each region were different, but in the 9 graphs measured the

time dependence of the ion counts in each region was converted to the number of counts per unit area. The diffusion coefficient of each region was obtained by curve fitting with Fick's law equation to the time evolution curves of hydrogen ions of these 9 graphs. The time evolution of the number of hydrogen ions in region H could be fitted with a single curve. On the other hand, region C could not be fitted on one curve but two curves, so we named these two components component 1 and component 2, respectively. From the ratio of the austenite structure and the martensite structure in each region, and from the magnitude of the diffusion coefficient calculated from the fitting curve, we regarded that the component 1 is hydrogen diffusion derived from the austenite structure, and the component 2 is hydrogen diffusion derived from the martensite structure (figure2(b)). On the other hand, in region X marked "unknown", the austenite structure and martensite structure were not clearly confirmed in IPF maps. The diffusion coefficient of hydrogen in this region was similar to martensite, but the permeation flux was comparable to austenite. After reconfirming with high resolution EBSD, it was found that there is a corresponding grain boundary of  $\Sigma 3$  at this location [3].

The diffusion coefficient as a function of the structural balance could be explained by a simple model of two coexisting structures. We know the martensite phases appeared as lath-like structures that were too fine for their crystal orientations to be identified. The austenite dominant region has two components of hydrogen diffusion, while martensite dominant region has only one component. When the martensite percentage is low, hydrogen supplied from the bottom surface will diffuse through only the austenitic phase or only the martensite phase as it penetrates to the upper surface. On the other hand, when the martensite percentage is high, the austenite phase becomes fragmented by interspersed lath-like martensite phases, and hydrogen supplied from the bottom surface cannot diffuse only in the austenite phase to the upper surface [5].



**Figure 2.** (a) Time evolution of hydrogen ion count in selected region. (b) Diffusion coefficient as a function of martensite percentage.

#### References:

- [1] T. Goto, et al., *Surface Science* **287/288** (1993), p361. doi: 10.1016/0167-2584(93)90452-0
- [2] N. Miyauchi, et al., *Scripta Materialia* **144** (2018), p69. doi:10.1016/j.scriptamat.2017.09.026
- [3] N. Miyauchi, et al., *Applied Surface Science* **527** (2020), p146710. doi:10.1016/j.apsusc.2020.146710
- [4] N. Miyauchi, et al., *Applied Surface Science* **492** (2019), p280. doi:10.1016/j.apsusc.2019.06.172
- [5] A. N. Itakura, et al., *Scientific Reports* **11** (2021), p8553. doi:10.1038/s41598-021-87727-5