In situ observations of silver-decoration evolution under hydrogen permeation: effects of grain boundary misorientation on hydrogen flux in pure iron

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Abstract

An in situ silver decoration technique using a light microscope was developed. Hydrogen was introduced from the bottom surface of an annealed pure iron specimen, and its top surface was covered with a chemical solution containing silver ions. Samples were exposed for sufficient time for hydrogen permeation to occur from the back to the top surface. The resultant in situ silver decoration visualized that the hydrogen flux through low-angle grain boundaries is lower than that observed at high-angle grain boundaries. The in situ silver decoration technique can be used for kinetic analysis of solute hydrogen in ferritic iron and steels.

Keywords: Silver decoration; Hydrogen; In situ observation; Pure Iron; Grain boundary misorientation

There is a high demand for the visual clarification of microstructural hydrogen diffusion and distribution kinetics in order to gain a quantitative understanding of hydrogen embrittlement mechanisms. For instance, hydrogen-assisted cracking occurs at specific grain/phase boundaries [1-4]. The factors causing the cracking are preferential diffusion and the segregation of hydrogen on or in the vicinity of the grain boundaries. Hydrogen visualization is required to correlate the cracking events with the presence of local hydrogen.

For hydrogen visualization, most of the recent technological efforts have been focused on three specific topics: quantification of the local hydrogen content [5-7], multi-scale hydrogen distribution observations [8, 9], and kinetically resolved hydrogen mapping [10-12]. In recent studies [12-14], scanning Kelvin probe force microscopy (SKPFM) has been reported to enable sequential kinetic analysis of microstructural hydrogen diffusion/segregation. SKPFM shows great advantages including a high spatial resolution and the availability of kinetic analysis for a long time range, for example, from over 5 hours to ideally infinite time. SKPFM is a powerful tool to kinetically resolve hydrogen diffusion-related events in strong hydrogen trap sites. In addition, the silver decoration technique has been noted as a complimentary method for SKPFM, as silver decoration enables hydrogen mapping over a short time range, e.g., within a few hours in ferritic steels. Hydrogen diffusion/segregation at weak trap sites can, therefore, be visualized by silver decoration [8]. Moreover, multi-scale hydrogen mapping is easily enabled through the use of light microscopy and scanning electron microscopy on the silver-decorated surface [8]. The observed results were demonstrated to have a significant correlation with damage initiation sites [9, 12, 15]. Despite the usefulness of silver decoration for the detection of hydrogen at weak trap sites, it has not been utilized to clarify the sequential process of hydrogen diffusion/segregation. In this paper, we present a methodology for in situ silver decoration under hydrogen permeation that yields results over a short time range. Furthermore, we report the dependence of hydrogen flux on grain boundary misorientation during the in situ silver decoration study.

The silver decoration technique is based on the following redox reaction between absorbed hydrogen atoms and silver ions at the interface between the metal surface and the solution [16].

As the reaction progresses, silver ions are reduced by absorbed hydrogen and metallic silver covers the area, which corresponds to the distribution of diffusible hydrogen. Silver deposition on a pure iron specimen surface has been clarified to stem from hydrogen evolution, and its detailed behavior such as an effect of applied potential has been characterized through electrochemical analysis elsewhere [17, 18]. In previous studies, the authors have demonstrated the silver decoration technique for fracture surfaces [19] and microstructural interfaces [8]. For a sake of clarify, in this study, the in situ silver decoration experiment was carried out under hydrogen permeation. A schematic for the setup for the in situ silver decoration is given in Fig. 1. The top surface of the specimen was immersed in a 4.3 mM potassium silver cyanide aqueous solution. Hydrogen was introduced by electrochemical charging of the bottom surface of the specimen using a current density of 6 A m^{-2} , at a temperature of 295 K and contained within a 3% sodium chloride aqueous solution, containing 3 g/L of ammonium thiocyanate. A platinum wire was used as the counter

electrode. The redox reaction occurs after hydrogen permeates through the specimen. A long focal distance optical lens was used to enable in situ observations of the specimen top surface without contact with the potassium silver cyanide aqueous solution. A 99.99% pure iron (wt.%) plate with a thickness of 0.34 mm was used as the specimen. The as-received pure iron plate was annealed at 1123 K for 0.5 h in a vacuum. The specimen surface was mechanically polished with a 60 nm colloidal silica paste. To analyze the correlation between the grain boundary misorientations and the silver decoration results, an electron backscattering diffraction pattern (EBSD) measurement was conducted at the identical location at an acceleration voltage of 15 kV with a beam step size of 4 μm . The EBSD specimen was slightly mechanically polished after the in situ experiment.

Figure 2 shows the optical micrographs recorded during the in situ experiment. The number of black dots was observed to increase with time. Specifically, the black dots initially appeared preferentially along the grain boundaries. Then they appeared also in the grain interior, although the distribution of the black dots was inhomogeneous in the grain interiors. All grain boundaries were fully occupied by the black dots after 90 minutes. These dots are observed as spherical particles in a secondary electron image (Fig. 3a) and have been reported to be metallic silver particles [9, 20, 21]. The black dots in the optical micrographs resulted from the redox reaction between the permeated hydrogen atoms and silver ions in the solution. Specifically, the silver-decorated region indicates a microstructural location that has a high flux of hydrogen. The silver decorated regions can be binarized clearly, as shown in Figs. 3b and 3c, which show clearly that grain boundaries are the sites with maximum hydrogen flux. The preferential silver deposition did not occur when hydrogen charging was not performed during the in situ observation (A video datum for a clearer comparison between the experiments with and without hydrogen charging is shown as a supplementary file).

Here, we discuss two points in the results of in situ silver decoration: (1) relationship between grain boundary misorientation and hydrogen flux and (2) delayed silver decoration (in fact, hydrogen atoms can penetrate the specimen within 20 s as discussed later.). First, note that some of the grain boundaries did not show a significant amount of silver particles before 90 minutes. A distinct example is seen in the binarized image of Fig. 3b. Since the specimen is an annealed polycrystalline pure iron, grain boundary misorientation is the most plausible factor causing the inhomogeneous distribution of silver particles. The corresponding grain boundary misorientation map, obtained by EBSD, is shown in Fig. 4a. As shown in Fig. 4b, a relationship between the silver decoration behavior and the grain boundary misorientation is obtained from the binarized images and the EBSD map. It is clearly shown that the degree of silver decoration on the low angle grain boundaries is significantly lower than that on relatively high angle grain boundaries. Hydrogen flux along low angle grain boundaries is, therefore, lower than that along the high angle grain boundaries.

To explain the relatively low flux of hydrogen through the low angle grain boundaries, we must understand the characteristics of detectable hydrogen by the silver decoration technique. The most important parameter causing the redox reaction between hydrogen atoms and silver ions is the flux of hydrogen, not only the diffusion rate. The steady-state permeation flux is given in equation 2 [22]

$$J = \frac{DC}{a}(\sqrt{P_1} - \sqrt{P_0}) \quad (2)$$

where D is the diffusion coefficient of hydrogen, C is the solubility coefficient, a is the thickness of the specimen, P_1 and P_0 are the hydrogen partial pressures at the entrance and exit surfaces, respectively. The hydrogen flux is determined by a combined effect of its solubility and local diffusion rate. From a viewpoint of diffusion rate, the diffusion length, L , can be obtained with the following equation.

$$L = \sqrt{Dt} \quad (3)$$

where t is the diffusion time. The diffusion coefficient of hydrogen in a polycrystalline pure iron at 295 K is $7.2 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ [23]. Hydrogen can, therefore, permeate through the full thickness (0.34 mm) of the specimen within 20 s. However, the silver deposition was observed to start after hydrogen charging for 30 minutes. Moreover, through hydrogen permeation tests in single and polycrystalline pure iron specimens, grain boundaries have been clarified to play no role in changing the diffusivity of pure iron at temperatures ranging from 270 K to 300 K [23]. These facts indicate that the silver particle distribution shown in Fig. 3 cannot be explained by a difference in the diffusion rate of hydrogen between the grain interior and grain boundary. In other words, the early hydrogen permeation through grain interior of the pure iron is not detected in the present technique in a statistically representative manner. More specifically, even if time-integrated amount of diffused hydrogen is high, the present silver decoration method may not be able to visualize distribution of low hydrogen flux such as that in grain interior of the annealed pure iron. Grain boundaries act as hydrogen trap sites [24] and have a higher capacity of hydrogen enrichment than the interstitial site in pure iron [25]. The segregation and accumulation of hydrogen at grain boundaries increase the hydrogen flux as schematically shown in Figs. 4c - 4e. The segregation process must, therefore, require a longer time than that required for permeation through the full specimen thickness. To be more specific, when we deal with local enrichment of hydrogen during hydrogen permeation, a competitive phenomenon of hydrogen motion must be considered. Hydrogen segregates to grain boundaries through diffusion, but also diffuses out to another grain interior/boundary or surface. The former increases local hydrogen content but the latter decreases. Therefore, a difference between the former and latter factors determines a degree of local hydrogen enrichment. A previous work [26] reported that hydrogen diffusivity of α -iron depends on grain boundary character that is different from a bulk diffusivity. However, the bulk diffusivity of a pure iron specimen has been experimentally found to be independent of existence of grain boundaries at ambient temperature [23]. These facts indicate that the difference in hydrogen diffusivity between grain boundary and grain interior is small, compared to an absolute value of bulk diffusivity. Accordingly, hydrogen existing on grain boundaries can diffuse out rapidly like the diffusion in grain interior. Hence, an evolution rate of local hydrogen enrichment at grain boundaries would be low. In other words, significant enrichment of hydrogen needs a longer time compared to hydrogen diffusion through specimen thickness.

In terms of the grain boundary misorientation dependence of the hydrogen flux, the local geometric structure of the grain boundaries affect the solubility [26]. Furthermore, hydrogen can

accumulate at lattice defects, and its degree depends on lattice defect density. Since low angle grain boundaries have a lower misfit and grain boundary dislocation densities, a limit of the local hydrogen enrichment would be lower than that for high angle grain boundaries. Note again that silver deposition rate depends on hydrogen flux that is determined by diffusivity and concentration of hydrogen at the corresponding location. Thus, the silver deposition on low angle grain boundaries was delayed because of the relatively low hydrogen flux at these locations.

In contrast to SKPFM enabling long-time kinetic analysis with the high spatial resolution, high sensitivity against hydrogen content, the in situ silver decoration technique presented here can work for short-time kinetic analysis with a large field of view and high statistical reliability. The complementary relationship indicates an importance of a combined approach of SKPFM and silver decoration technique.

In this study, we successfully demonstrated the silver decoration technique for the in situ characterization of hydrogen flux distribution of pure iron. Silver deposition occurred preferentially on grain boundaries. However, low angle grain boundaries showed a delay of silver deposition. The silver particle distribution on the pure iron surface corresponds to the local hydrogen enrichment that results in a difference in the hydrogen flux. The delay in silver deposition at low angle grain boundaries indicates relatively low capacity of the local hydrogen enrichment compared with that for high angle grain boundaries. An advantage of the in situ technique is regarding the continuous detection of hydrogen that is diffusible even at ambient temperature. Since hydrogen charging and subsequent aging in the solution can also cause silver deposition, what ex situ silver decoration approach visualizes may have intrinsically different elements of the nature of hydrogen distribution. Namely, the present in situ technique has a great advantage for visualizing an underlying behavior of hydrogen permeation and subsequent desorption.

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Figure 1. A schematic for the setup of the in situ silver decoration.

Figure 2. Results of the light microscopy observations during the hydrogen permeation testing at (a) 0, (b) 30, (c) 53, (d) 55, (e) 60, and (f) 90 minutes.

Figure 3. (a) Secondary electron image corresponding to the region outlined in Fig. 2(f). Digitally binarized images of the optical micrograph at (b) 53 and (c) 90 minutes.

Figure 4 (a) EBSD grain boundary map. The black arrows indicate low angle grain boundaries ($0^\circ < \theta < 15^\circ$). (b) The fraction of silver decorated grain boundaries plotted against grain misorientation. Schematics for the change in hydrogen diffusion/segregation and associated change in flux: (c) hydrogen entry immediately after hydrogen charging, (d) hydrogen distribution after hydrogen diffusion through the full thickness of the specimen, and (e) hydrogen segregation at grain boundaries and a subsequent increase in local hydrogen flux. The width of the arrows indicates the hydrogen flux. Blue and grey circles indicate hydrogen and silver atoms, respectively.

Figure 1

Figure 2

Figure 3

Figure 4

In situ silver decoration

55 min

90 min

Grain boundary misorientation dependence of hydrogen flux

Binarized optical image + EBSD