Detection of Hydrogen Distribution in Pure Iron Using WO₃ Thin Film

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(Received on April 3, 2018; accepted on May 31, 2018)

The usefulness of a new approach to detecting the distribution of hydrogen absorbed into pure iron utilizing a WO₃ thin film was demonstrated in this study. A WO₃ film with an electrochromic property was formed on the hydrogen detection side of iron sheet by reactive magnetron sputtering. After hydrogen was absorbed into the iron sheet by cathodic polarization on the hydrogen absorption side, the color of the WO₃ film corresponding to the electrode area changed from light blue to dark blue. The WO₃ film was found to reflect the distribution of hydrogen absorbed into the pure iron sheet. No color change occurred on the hydrogen detection side unless a Pd film was inserted between the WO₃ film and the iron specimen. The reflectance of the WO₃ film in the visible region was reduced by hydrogen charging, with a marked reduction in the RGB color values after the start of hydrogen charging. The results of an XPS analysis suggested that the phase transition from WO₃ to HₓWO₃ resulted in the color change of the WO₃ film during hydrogen charging. Because of the simplicity of this approach to detecting hydrogen compared to other hydrogen detection methods, it is expected to have various applications.

KEY WORDS: WO₃ thin film; hydrogen detection; hydrogen mapping; electrochromic reaction; reactive magnetron sputtering; pure iron.

1. Introduction

Hydrogen embrittlement (HE) is a serious problem for high strength steels. It is well-known that high strength steel bolts suffer from delayed fracture in atmospheric corrosion environments.¹⁻³ Under atmospheric exposure, hydrogen absorption into steel occurs as a result of the cathodic reaction during the corrosion process. The hydrogen atoms produced by the cathodic reaction are adsorbed on the steel surface, and a small quantity of the adsorbed atoms are absorbed into the steel matrix.⁴⁻⁶ The accumulation of hydrogen in steel results in delayed fracture, and the susceptibility of HE increases with an increase in the strength of steels.⁷ The material design to prevent high strength steel bolts from delayed fracture has been studied: vanadium-containing steels have been reported to have a high resistance to HE.⁸ Besides the strategy to reduce the risk of HE by the material design, a method to inhibit hydrogen absorption into steel during atmospheric corrosion is required to ensure the safe and widespread use of high strength steels. Because hydrogen absorption behavior is deeply sensitive to surface heterogeneity, a real-time observation method for obtaining the distribution of the hydrogen absorbed at the steel surface is needed.

The combined effect of the low solubility limit of hydrogen in steels and the high diffusivity of hydrogen to escape from steels at room temperature makes it difficult to detect hydrogen in steels.⁹ This explains the distinct lack of methods available for the detection of hydrogen. The electrochemical hydrogen permeation technique developed by Devanathan et al. is effective in evaluating the hydrogen permeation rate and the diffusion coefficient of hydrogen.¹⁰,¹¹ The thermal desorption analysis is useful in obtaining the solubility and the existing states of hydrogen in steels.¹²,¹³ However, neither of these methods is capable of observing the distribution of the absorbed hydrogen. The hydrogen microprint technique¹⁴,¹⁵ and the silver decoration¹⁶,¹⁷ method are established methods to obtain the distribution of hydrogen near the steel surface. In addition, secondary ion mass spectrometry¹⁸,¹⁹ and the three-dimensional atom probe²⁰ are capable of detecting local hydrogen with a high spatial resolution. However, neither of these methods is capable of measuring temporal changes in the distribution of the absorbed hydrogen.

Though scanning electrochemical microscopy²¹ and scanning laser-enhanced electrochemical microscopy²² have been reported as in situ visualizing methods for determining the distribution of hydrogen on steel surfaces, few reports have appeared in the literature to date. It should be noted that a
surface potential mapping using a scanning Kelvin probe (SKP) or Kelvin probe force microscopy (KPFM) is being established as an in situ hydrogen mapping technique.\textsuperscript{23–28} It is known that the work function changes by the adsorption of hydrogen on the surface of iron.\textsuperscript{29} This knowledge has been applied to hydrogen mapping, and the dependence of hydrogen trapping on microstructure heterogeneity have been extensively studied. Senoz et al. employed KPFM to measure a surface potential of a duplex steel subjected to hydrogen charging, and revealed that ferrite grains showed a large change in the surface potential than austenite ones.\textsuperscript{30} This potential change was explained by the difference of the hydrogen diffusivity between austenite and ferrite.\textsuperscript{31} Koyama et al. tried the detection of hydrogen distribution for a twinning-induced austenitic steel after hydrogen charging from the viewpoint of the surface potential obtained by KPFM, and suggested that hydrogen localization occurs at deformation twins.\textsuperscript{32} The change in the distribution of hydrogen due to corrosion was also observed by SKP. Schaller et al. showed that the hydrogen distribution of a cross section of a Fe–Cr–Ni–Mo steel was mapped by SKP after pitting.\textsuperscript{33} While the SKP and the KPFM are powerful tools for the real-time mapping of hydrogen absorbed into steels experimentally, it should be difficult that these techniques are used in outdoor environments. In order to monitor the distribution of the hydrogen absorbed into steels in atmospheric corrosion environments, simpler methods are required.

We tried to measure the distribution of hydrogen absorbed into pure iron using a WO\textsubscript{3} thin film. WO\textsubscript{3} is well-known as electrochromic material. The formation of H\textsubscript{x}WO\textsubscript{3} by the reduction of WO\textsubscript{3} leads to the change in the optical property of WO\textsubscript{3}.\textsuperscript{33,34} We drew inspiration from this electrochromic property of WO\textsubscript{3}, and focused on the color change associated with the phase transition from WO\textsubscript{3} to H\textsubscript{x}WO\textsubscript{3} as a method for detecting the hydrogen distribution in iron. Our approach to detecting hydrogen absorbed into an iron sheet is to contact a WO\textsubscript{3} thin film with the iron sheet via a Pd thin film. If hydrogen is absorbed into the iron sheet and is diffused into the WO\textsubscript{3} thin film, the optical property of the WO\textsubscript{3} film is expected to change due to the formation of H\textsubscript{x}WO\textsubscript{3}. The objective in this study was to demonstrate the approach to detecting the real-time distribution of hydrogen absorbed into pure iron using a WO\textsubscript{3} thin film.

2. Experimental

2.1. Specimen and Electrolyte

Commercial pure iron sheet 1 mm in thickness was used as the specimen in this study. Table 1 shows the chemical composition of the iron specimen. Because the sulfur concentration was lower than 0.001 mass\%, the formation of sulfide inclusions such as MnS, which was reported to induce the hydrogen absorption,\textsuperscript{35–37} was inhibited. The pure iron sheet was cut into 25 mm × 25 mm coupons. All the iron specimens were heat-treated at 723 K for 18 ks to remove hydrogen, and were then furnace-cooled. Before any electrochemical measurements and the deposition of WO\textsubscript{3}, the iron specimen surfaces were mechanically ground with SiC papers through a 1 500 grit, mirror-polished with a 1 \(\mu\)m diamond paste, and ultrasonically cleaned with ethanol.

Electrochemical measurements were performed in a naturally aerated 0.1 M H\textsubscript{2}SO\textsubscript{4} solution at 298 K. The solutions were prepared using deionized water and analytical grade sulfuric acid.

2.2. WO\textsubscript{3} Film Formation

The substrates were a slide glass, an indium tin oxide-deposited glass (ITO glass), and a pure iron specimen. The slide glass and the ITO glass were ultrasonically cleaned with ethanol prior to WO\textsubscript{3} deposition. A Pd thin film 80 nm in thickness was electrochemically coated on the hydrogen detection side of the iron specimen. The Pd electrodeposition was conducted in the constant current mode at 100 A m\textsuperscript{−2} for 60 s. The plating bath consisted of 2.0 g L\textsuperscript{−1} Pd(NH\textsubscript{3})\textsubscript{4}(NO\textsubscript{2})\textsubscript{2}, 24 mg L\textsuperscript{−1} aqueous NH\textsubscript{3} (28 mass\%), and 95 g L\textsuperscript{−1} (NH\textsubscript{4})\textsubscript{2}HPO\textsubscript{4}. The solution was kept at 298 K and was agitation at 5 s\textsuperscript{−1} during the Pd electrodeposition. The Pd-coated region was a ca. 15 mm square. After the surface was electrochemically coated with Pd, the WO\textsubscript{3} deposition was conducted.

The WO\textsubscript{3} thin film was formed by a magnetron sputter system. A reactive radio frequency (RF) sputtering\textsuperscript{38} was conducted in a mixed Ar/O\textsubscript{2} discharge. The target was a W disc 50.8 mm in diameter, its purity was 99.95 mass\%. The distance between the substrate and the target was 70 mm. The substrate was heated at 573 K, and rotated at 5 rpm (rotations per minute) during the sputtering. Before the sputtering, the vacuum chamber of the sputtering system was evacuated to a pressure lower than 5 × 10\textsuperscript{−5} Pa, and Ar and O\textsubscript{2} gases were introduced into the chamber. The flow rates of Ar and O\textsubscript{2} gases were 1.7 × 10\textsuperscript{−7} and 8.3 × 10\textsuperscript{−8} m\textsuperscript{3} s\textsuperscript{−1}, respectively. Sputtering was carried out at a pressure of 4.5 Pa. The RF power was 50 W. Sputtering was continued for 5.2 ks, and the WO\textsubscript{3} film was 40 nm in thickness when sputtering was discontinued.

2.3. Cathodic Polarization Curve

A potentiodynamic cathodic polarization measurement of the pure iron specimen in 0.1 M H\textsubscript{2}SO\textsubscript{4} was carried out using a conventional three electrode cell. A Pt plate was used as the counter electrode. An Ag/AgCl (3.33 M KCl) electrode was used as the reference electrode. In this paper, all the potential values refer to the standard hydrogen electrode (SHE). The potential scan rate was 0.38 mV s\textsuperscript{−1}. The electrode area was ca. 10 mm × 10 mm. The electrode region was limited by masking with an epoxy resin and then paraffin. The electrode area was scaled after the polarization measurement was conducted. The area was used to convert the measured current value to the current density.

2.4. Cyclic Voltammetry

The cyclic voltammetry of the WO\textsubscript{3} film formed on the ITO glass was carried out in 0.1 M H\textsubscript{2}SO\textsubscript{4} to evaluate its electrochromic properties. The counter electrode was a Pt
plate, and the reference electrode was an Ag/AgCl (3.33 M KCl) electrode. The specimen was sealed by a masking tape, with the exception of a working electrode region with dimensions of ca. 10 mm × 10 mm. The electrode was polarized at −0.3 V, and then a potential scan was started in the positive direction at 5 mV s⁻¹. The potential range of the voltammetry was from −0.3 to 1.2 V.

2.5 Hydrogen Charging and Detection Measurement

Detection of hydrogen on the iron specimen was tried using the WO₃ film. Figure 1(a) shows the schematic of the experimental setup for hydrogen charging and hydrogen detection with the WO₃ film. The left side of the iron specimen was contacted to an acrylic electrochemical cell for hydrogen absorption. The cell was sealed with an O-ring. The working electrode (W. E.) was the mirror-polished pure iron. The counter electrode (C. E.) was a Pt plate, and the reference electrode (R. E.) was an Ag/AgCl (3.33 M KCl) electrode. Potentiostatic polarization in 0.1 M H₂SO₄ was performed at −0.514 V for 43.2 ks for hydrogen charging. The surface of the WO₃ film during hydrogen charging was monitored by a high-resolution video camera. An O-ring was placed to avoid the interference of light arising between the probe and no other W species were detected. This clearly shows the protonation side of the iron specimen. The surface inside the O-ring was exposed to the solution. It is expected that many hydrogen bubbles were contacted on the upper side of the electrode surface during hydrogen charging. To remove the influence of residual hydrogen bubbles on hydrogen absorption, the upper side of the iron specimen was covered with masking tape. Therefore, the semicircular region without masking inside the O-ring corresponds to the electrode area for hydrogen charging.

2.6 Surface Observation and Analysis

The surface appearance of the WO₃ film was taken by a digital camera except the real-time observation by the video camera during hydrogen charging. When the surface of the WO₃ was observed by the digital camera, the WO₃ films on the ITO glass and the iron specimen were removed from the electrochemical cells. The thickness of the WO₃ and the Pd film was determined by a contact surface profiler. When WO₃ was sputtered on the slide glass, a part of the substrate was covered with a cover glass to form a non-sputtered area. After the sputtering, the difference in height from the non-sputtered area to the WO₃-sputtered area was measured by the surface profiler.

The reflectance measurements of the WO₃ film were carried out with a tungsten halogen light source coupled though an optical fiber. A reflection probe consisted of optical fibers that were connected to the light source and a spectrometer. The probe was located perpendicularly to the WO₃ film by a probe holder. The dependence of the reflectance on the wavelength was examined between 300 nm and 800 nm.

The formation of WO₃ and HₓWO₃ was confirmed by angular-resolved X-ray photoelectron spectroscopy (XPS). A monochromated Al-Kα radiation at an accelerating voltage of 15 kV and an anode current of 30 mA were employed. Because a spectrum with a high intensity is suitable for the deconvolution, the XPS spectra were calculated from the integration of the spectra obtained at a photoelectron-detection angle from 21.875 to 78.125°. The binding energy in the XPS spectra was calibrated based on the peak position of the C–H bond in the C 1s level (285.00 eV). In the case of the deconvolution, the synthesized and the deconvoluted spectra were exhibited after the background spectra were subtracted from the measured spectra by the Shirley method.

3 Results and Discussion

3.1 Characterization and Electrochromic Property of WO₃ Film

In order to identify the as-deposited film on the iron specimen formed by the reactive magnetron sputtering as WO₃, an XPS analysis was conducted. Figure 2 shows the measured, the synthesized, and the deconvoluted W 4f XPS spectra of the as-deposited film. The synthesized spectrum indicates two peaks at the binding energies of 36.3 and 38.4 eV. Because some reports showed the peaks of the W 4f½ and the W 4f¾ for WO₃ were located at the binding energies of ca. 36.2 and 38.3 eV, the deconvolution result indicates that the two peaks in the synthesized spectrum were assigned to the W 4f½ and the W 4f¾ for WO₃ and no other W species were detected. This clearly shows
that the surface of the as-deposited film formed by the reactive magnetron sputtering consisted of pure WO$_3$.

To be useful for hydrogen mapping, the WO$_3$ film is required to have an electrochromic property. The electrochromic property of the WO$_3$ film formed by the reactive magnetron sputtering was therefore examined by cyclic voltammetry in 0.1 M H$_2$SO$_4$ at 298 K. Figure 3 shows the cyclic voltammogram of the WO$_3$ film on an ITO glass measured at a scan rate of 5 mV s$^{-1}$. The cyclic voltammetry measurements were repeated for three cycles, and the last cycle of voltammogram was presented. The first and the second cycles of voltammograms were almost the same as the last cycle.

In the anodic scan from $-0.3$ to $1.2$ V, a large current peak was observed at $-0.1$ V, and the anodic current decreased with a rise in the potential. In the cathodic scan from $1.2$ to $0.2$ V, the cathodic current slightly increased with a drop in the potential, and dramatically increased at potentials below $0.2$ V. It appears that most of the anodic and the cathodic reactions occur in the potential range from $-0.3$ to $0.5$ V. Besides this, amounts of the anodic and the cathodic charges from $-0.3$ V to $1.2$ V are 80.0 and 80.1 C m$^{-2}$, respectively, suggesting that a reversible electrochemical reaction took place in the anodic and the cathodic scan, and the hydrogen evolution reaction was negligible. It has been reported that the following electrochromic reaction occurs on WO$_3$ in acidic solutions:

$$\text{WO}_x\text{H}_y\text{O}_z \rightleftharpoons \text{H}_x\text{WO}_3 \quad \text{(1)}$$

It is considered that the anodic and the cathodic currents observed in Fig. 3 were caused by this electrochromic reaction, because no electrochemical reaction on the surface of the ITO glass is likely to occur in the potential range from $-0.3$ to $1.2$ V in the acidic solution. Due to the reversible insertion and removal of H$^+$, the color of the WO$_3$ film is expected to alter after anodic and cathodic polarizations.

Figure 3(b) shows the surface appearance of the WO$_3$ film on the ITO glass at $-0.3$ V. This image was taken by the digital camera after the cathodic scan from $1.2$ to $-0.3$ V in the cyclic voltammetry. The WO$_3$ film was dark blue. The average RGB (red, green, blue) values for all pixels in this image were calculated to be ($R$, $G$, $B$) = (130, 142, 156), Standard deviation = (7.0, 7.1, 4.3). In this study, the range of the RGB values was from 0 to 255. The surface appearance of the WO$_3$ film at $1.2$ V is shown in Fig. 3(c). This image was taken after the anodic scan from $-0.3$ to $1.2$ V in the cyclic voltammetry. The WO$_3$ film was transparent, and its average RGB values were calculated to be ($R$, $G$, $B$) = (213, 212, 226), Standard deviation = (4.3, 4.1, 4.9). After the polarization at $-0.3$ V, the WO$_3$ film seemed to be reduced to H$_x$WO$_3$, and the RGB values decreased remarkably.

The cyclic voltammetry measurement shows the WO$_3$ film formed by the reactive magnetron sputtering has the electrochromic property. Therefore, the WO$_3$ film is expected to be an effective material for the use in hydrogen mapping.

**3.2. Cathodic Polarization Curve**

In order to determine the hydrogen charging condition, the cathodic polarization curve of the iron specimen was measured. Figure 4 shows the potentiodynamic cathodic polarization curve of the iron specimen in naturally aerated 0.1 M H$_2$SO$_4$ at 298 K. The potentiodynamic polarization started at $-0.29$ V. The corrosion potential was $-0.32$ V, and the cathodic current increased with decreasing potential. The cathodic current is attributed to the hydrogen evolution reaction. From the polarization curve, the potential for hydrogen charging in this study was set at $-0.514$ V because this potential corresponds to the current density of 100 A m$^{-2}$. 

$$\text{WO}_3 + x\text{H}^+ + x\text{e}^- \rightarrow \text{H}_x\text{WO}_3 \quad \text{(1)}$$
3.3. Color Change of WO₃ Film on Iron Specimen during Hydrogen Charging

Hydrogen charging at −0.514 V was conducted to the hydrogen absorption side of the iron specimen, and the surface of the WO₃ film on the hydrogen detection side of the iron specimen was observed. Figure 5(a) shows the appearance of the as-deposited WO₃ film on the iron specimen taken by the video camera. The light blue and square region inside the O-ring corresponds to the area where Pd was electrodeposited on the iron specimen, and WO₃ was subsequently deposited on the Pd film. Figure 5(b) shows the appearance of the WO₃ film after hydrogen charging for 43.2 ks. A dark blue and semicircular shape was clearly observed in the region coated with the Pd and the WO₃ film in Fig. 5(b).

Figure 6 shows the surface appearance of the hydrogen absorption and the detection sides of the iron specimen after hydrogen charging for 43.2 ks, and the pictures were taken by the digital camera. The picture of the hydrogen absorption side (Fig. 6(a)) was taken after the removal of the masking tape, and was horizontally flipped to correspond with that of the hydrogen detection side. The brown and semicircular shape observed on the hydrogen absorption side indicates the formation of corrosion products under open circuit conditions before and after hydrogen charging. This suggests that the brown and semicircular shape is equivalent to the electrode area. The dashed-line in Fig. 6(b) represents the electrode area for hydrogen charging. Since the dark blue and semicircular area observed in the WO₃ film was similar shape to the electrode area for hydrogen charging, it seems that the change in the color of the WO₃ film was brought about by the hydrogen atoms, which were absorbed into the iron specimen by hydrogen charging and were diffused to the WO₃ film.

In Figs. 5(b) and 6(b), the area outside the light blue and square region corresponds to the WO₃ film on the pure iron without Pd coating. The change in the color of the WO₃ film occurred only inside the blue and square region. This suggests that the Pd layer between the WO₃ film and the pure iron plays a key role in the color change of the WO₃ film. The role of Pd coating in hydrogen detection will be discussed in our next paper.

The change in the surface appearance of the WO₃ film in the dashed-line box in Fig. 5(b) during hydrogen charging is shown in Fig. 7. At the beginning of hydrogen charging, the surface of the WO₃ film was light blue, and no visible color changed for 3.6 ks. After 7.2 ks, the color around the center of the WO₃ film slightly changed to dark blue, and a semicircular shape gradually emerged as time went by. At 21.6 ks, the dark blue and semicircular shape was clearly observed at the center of the WO₃ film. Because the semicircular shape corresponds to the electrode area, the color change of the WO₃ film was thought to be attributed to the formation of HₓWO₃ due to the hydrogen atoms, which were absorbed into the iron specimen and were diffused to the WO₃ film. After 21.6 ks, the color change expanded outside the electrode area. Because the hydrogen atoms absorbed from the electrode area diffuse through the iron specimen radially, the semicircular shape became larger with time.
3.4. Optical Property Change of WO₃ Film

The results presented so far indicate that it is possible for a WO₃ film to form a real-time mapping of hydrogen absorbed into pure iron sheet. In order to discuss the change in the optical property of the WO₃ film, the reflectance spectrum in the visible region was measured at Points A and B in Fig. 5.

Figure 8 shows the reflectance spectra of the WO₃ films before and after hydrogen charging. The reflectance of the as-deposited WO₃ film increased in the wavelength region of 300–400 nm, with a maximum value observed around 400 nm. In the wavelength region of more than 400 nm, the reflectance gradually decreased with the increase in the wavelength. The local minimum value was recognized at the wavelength of 670 nm, and the reflectance increased with the increase in the wavelength. Because the band gap of WO₃ was ca. 2.7 eV (wavelength: 459 nm), the increase in the reflectance in the wavelength region of 300–400 nm is likely to be due to interband transition. In addition, the reflectance shift in the wavelength region of more than 400 nm seems to be caused by light interference. Since the maximum value of the reflectance was located in the violet and blue region (wavelength: 400–480 nm), the color of the as-deposited WO₃ film appeared light blue.

In the case of the WO₃ film after hydrogen charging, the reflectance was smaller in the visible region (wavelength: 380–780 nm). Since the wavelength inducing a maximum reflectance value after hydrogen charging was similar to that for the as-deposited WO₃, the WO₃ film seems to change in color to dark blue. Because the hydrogen absorption decreases the reflectance of the WO₃ film in the visible region, the change in the color of the WO₃ film can be evaluated using the RGB color chart.

Figure 9 shows the time variations of the RGB values of the WO₃ film at Point C in Fig. 7. All the color values dramatically decreased once hydrogen charging was started, with the most distinct change occurring in the R value. Even though the color change between 0 to 3.6 ks could not be visibly observed in Fig. 7, a clear change in the RGB values could be recognized. This suggests that by referring to the RGB color chart, the WO₃ film can be used to detect even a small amount of absorbed hydrogen.

3.5. XPS Analysis for Mechanism of Change in Color of WO₃ Film

Finally, in order to investigate the reason for the change in the color of the WO₃ film, an XPS analysis was conducted before and after hydrogen charging. Figure 10(a) shows the W 4f XPS spectra of the WO₃ film before and after hydrogen charging. For the as-deposited WO₃ film, two peaks were observed at the binding energies of 36.4 and 38.5 eV. The spectrum of the WO₃ film after hydrogen charging also exhibited two peaks at the binding energies of 36.6 and 38.5 eV. These peaks are assigned to the W 4f₋₂ and the W 4f₋₃/₂, respectively. After hydrogen charging, one of the peaks shifted to a higher binding energy. In addition, the peaks of the WO₃ film after hydrogen charging became broader than those of the as-deposited one. Figure 10(b)
Fig. 10. (a) W 4f and (b) O 1s XPS spectra obtained on WO3 film before and after hydrogen charging. (c) Measured, synthesized, and deconvoluted W 4f XPS spectra of the WO3 film after hydrogen charging.

shows the O 1s XPS spectra of the WO3 film before and after hydrogen charging. Peaks were observed from the O 1s XPS spectra: 531.3 eV for the as-deposited WO3 film and 531.5 eV for the WO3 film after hydrogen charging, respectively. The O 1s XPS spectra also exhibit that a peak shift occurred, and that the peak became broader due to hydrogen charging. These results suggest that the electronic structure of the WO3 film changed due to hydrogen absorbed into the iron specimen and diffused into WO3. Barreca et al. reported the similar peak shift of the W 4f XPS spectrum of a mixed phase WOx (2<x<3) film.49)

Because of the likelihood that contamination species, such as H2O, adsorb on the surface of the WO3 film, it is difficult to analyze the electronic structure from the O 1s XPS spectra. Therefore, the deconvolution analysis of the W 4f XPS spectra was performed. The deconvolution spectrum in Fig. 2 indicates that the as-deposited film is pure WO3. The measured, the synthesized, and the deconvoluted W 4f XPS spectra of the WO3 film after hydrogen charging are shown in Fig. 10(c). The binding energies for the peaks of the W 4f x2 and the W 4f x2 for WO3 (2<x<3) were determined based on the reference data for WO2.50) The synthesized spectrum after hydrogen absorption was deconvoluted into four peaks for WO3 and WOx (2<x<3), suggesting that the WO3 film after hydrogen charging contained HxWO3. It is likely that hydrogen atoms absorbed from the hydrogen absorption side reduce the WO3 film, and HxWO3 was formed. The phase transition from WO3 to HxWO3 seems to result in the color change of the WO3 film during hydrogen charging.

A new approach to detecting the distribution of hydrogen absorbed into pure iron and steels which utilizes the phase transition from WO3 to HxWO3 was proposed in this study. Because only WO3 and Pd layers are coated on the hydrogen detection side, detecting absorbed hydrogen become simpler than the other hydrogen detection methods reported to date. It is likely that this approach to detecting absorbed hydrogen can be applied for various purposes, such as hydrogen mapping for living steel structures and the detection of hydrogen absorbed by atmospheric corrosion. Further studies are needed to improve the spatial resolution and the detection sensitivity.

4. Conclusions

(1) The pure WO3 film could be formed on a slide glass, an ITO glass, and a pure iron specimen by the reactive magnetron sputtering. This WO3 film had an electrochromic property.

(2) The WO3 film was formed on the hydrogen detection side of the iron specimen. During hydrogen charging, the color of the WO3 film gradually changed from light blue to dark blue in the electrode area. This suggests that the WO3 film can be used to map the hydrogen absorbed into pure iron sheet. No change in the color in the hydrogen detection side occurs unless a Pd film was inserted between the WO3 film and the iron specimen.

(3) Hydrogen absorption decreases the reflectance of the WO3 film in the visible region. All the RGB color values dramatically decreased after the start of hydrogen charging.

(4) The phase transition from WO3 to HxWO3 seems to lead to the change in the color of the WO3 film during hydrogen charging.

(5) The usefulness of an approach to detecting the distribution of hydrogen absorbed into pure iron and steels using WO3 was successfully demonstrated in this study.
Acknowledgments

This work was performed under the support of a Grant-in-Aid for Challenging Exploratory Research from Japan Society for the Promotion of Science (grant No. 26630357) and the ISIJ Research Promotion Grant from The Iron and Steel Institute of Japan.

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