Graphene coating as a protective barrier against hydrogen embrittlement

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Abstract
The applicability of a graphene coating as a protective barrier against hydrogen embrittlement was studied. To simulate the hydrogen embrittlement, complex environment of tensile stress with simultaneous hydrogen charging was applied. The strain at fracture, ductility and ultimate tensile strength of graphene-coated copper under the charged condition were preserved above 95% comparing uncharged bare copper. After hydrogen charging for 12 h, the hydrogen content in graphene-coated copper was lower than that in bare copper. Using attenuated total reflectance infrared spectroscopy and Raman spectroscopy, it was verified that graphene can interrupt the hydrogen penetration by the formation of C–H sp³ bonds. Unfortunately, it induced a distortion of graphene structure, which increased the defects in the graphene. Nevertheless, the graphene coating is expected to decrease the hydrogen embrittlement susceptibility of metal substrate.

Introduction
The effect of hydrogen on the mechanical properties of metals is known as hydrogen embrittlement (HE), which can cause catastrophic failures [1]. HE has been an important issue in various applications, such as reactor vessels in nuclear plants [2,3], high-pressure gaseous hydrogen (HPGH₂) storage tanks [4,5], and pipelines for natural gas and petroleum [6,7]. There are two mechanisms of HE in metals. One is that the atomic hydrogen is attracted to crack tips, and reduces the fracture energy while encouraging cleavage-like failure [8,9]. The other mechanism involves atomic hydrogen enhancing the mobility of dislocations through an elastic shielding effect, causing locally reduced shear strength, and eventually enhancing the local plasticity [10]. Although there is a difference in reaction process of hydrogen, it is distinct that HE is induced by interaction between internal hydrogen and external tensile stress. Therefore, in order to reduce the potential risk of hydrogen embrittlement, or to protect metal from hydrogen permeation, several methods have been proposed, including heat treatment [11], neon/helium glow discharge [12], inhibitors of hydrogen permeation [13], and protective barriers of zirconium dioxide [14]. However, the limitations of these methods include bulky thickness, toxic substance usage, relatively low inhibition efficiency, and detrimental effects on the matrix materials. Recently, we report new methods for eliminating the hydrogen inside low alloy steel by
Graphene possesses various unique properties that are suitable for protective barriers of metal against hydrogen permeation. Graphene is impermeable to gas molecules [17]. Hydrogen is also adsorbed on graphene surfaces as $sp^3$ C–H bonds [18–20], which enables the viability of graphene for hydrogen storage [21,22]. Additionally, graphene is chemically stable in ambient atmosphere at up to $400 \text{ }^\circ \text{C}$ [23], and can protect the underlying metal substrate from corrosion [24,25] and oxidation [26]. Also, growth techniques for large-area graphene film are being developed, which will enable the commercial applicability of graphene [27]. However, graphene has not been studied as a protective barrier against HE. Especially, under applied stress and hydrogen charge simulating HE condition, the effect of graphene on the mechanical properties of bulky metal has not also been investigated.

In this study, the applicability of graphene as a protective barrier against HE is investigated. Graphene was coated onto a copper substrate by chemical vapor deposition (CVD). The mechanical properties of specimens were assessed by slow strain rate tests (SSRTs) under tensile stress with simultaneous hydrogen charging. In order to quantitatively evaluate the susceptibility of specimen to the HE, the hydrogen embrittlement ratio (HER, \%) was calculated. The actual protective efficiency of graphene for hydrogen permeation was evaluated by measuring the content of hydrogen inside of a specimen using gas chromatography (GC). The effect of graphene on the mechanical properties of bulky metal has not also been investigated.

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**Material and methods**

**Graphene preparation**

For the synthesis of graphene by chemical vapor deposition (CVD), copper foil (70 \text{ \mu \text{m}}, purity 99.9\%) was placed into a quartz tube. The specimen was annealed at $1050 \text{ }^\circ \text{C}$ under H$_2$. A gas mixture of CH$_4$ (20 sccm) and H$_2$ (10 sccm) was flowed into the quartz tube for the growth of graphene under 10 Torr. After 30 min, the chamber was cooled down to room temperature under H$_2$.

**Hydrogen charging**

Cathodic charging is used to introduce hydrogen into a specimen. The use of so-called poisons in the electrolyte is applied to hinder the H$_2$ formation and to consequently improve the hydrogen absorption. Arsenic-based poisons such as As$_2$O$_3$ are used in sulfuric acid during hydrogen charging [28]. Before the experiment, nitrogen gas was bubbled into the solution for 2 h to exclude the influence of oxygen. To charge the hydrogen, the galvanostatic test is performed at $-1.0 \text{ mA/cm}^2$ for 12 h. A solution of 0.5 M sulfuric acid ($H_2SO_4$) + 250 mg/L arsenic trioxide (As$_2$O$_3$) (pH = 1.0) was used to control the hydrogen formation and to ease the percolation and diffusion of the hydrogen atoms into the specimen.

**Slow strain rate tests (SSRTs)**

To identify the effect of graphene as a hydrogen diffusion barrier on the mechanical properties of a specimen, slow strain rate tests (SSRTs) are conducted at a constant strain rate of $1.0 \times 10^{-6}$/s. This test is extensively used to evaluate the resistance of a material to HE and stress corrosion cracking [29,30]. A schematic picture of the test setup was presented (Fig. 1a). Cylindrical tensile specimens are fabricated according to NACE Standard TM0177 and have threaded ends with a diameter of 6.35 mm and a gauge length of 25.4 mm. Except for the gauge length, the specimens are coated with insulating lacquer to make the exposed surface areas identical. The specimen is connected to pull-rods, and the load and elongation are monitored continuously by a load cell and a linear variable differential transformer (LVDT) until fracture occurs. During the SSRT, hydrogen is charged until failure occurs. By applying complex conditions of hydrogen charge and tensile stress, the susceptibility of the metal to HE can be evaluated.

**Hydrogen content measurement**

Hydrogen is electrochemically charged for 12 h, and then the amount of hydrogen accumulated inside the specimen is measured by gas chromatography in the temperature range of 50–500 °C. The hydrogen charged specimens are introduced to a thermostat-controlled furnace and held under inert argon purge. A constant heating rate of 10 °C/min is applied, and the amount of hydrogen evolved is measured.

**Cathodic polarization**

An EG&G PAR Model 273A potentiostat was used for electrochemical polarization tests which were conducted using a conventional three-electrode system. The test specimen was used as the working electrode, a saturated calomel electrode (SCE) was used as the reference electrode, and graphite was used as an auxiliary electrode. A solution of 0.5 M sulfuric acid ($H_2SO_4$) + 250 mg/L arsenic trioxide (As$_2$O$_3$) (pH = 1.0) was used. Before the experiment, nitrogen gas was bubbled into the solution for 2 h to exclude the influence of oxygen. Cathodic polarization tests were performed at a scanning rate of 0.166 mVSCE from +50 mVOCV to −1200 mVSCC.

**Characterization of graphene**

The hydrogen charged and uncharged graphene was transferred onto Si wafer (SiO$_2$300 nm)/Si by the polymethyl methacrylate (PMMA) for Raman spectroscopy and atomic force microscopy (AFM) analyses. First, the PMMA was coated on graphene/Cu samples as a supporting layer. The copper foil was etched by copper etchant (Sigma–Aldrich Korea Ltd., 3–4% of HCl, 30% of FeCl$_3$, 66–67% of water) and the PMMA/graphene transferred onto the wafer. Finally, the PMMA was removed by acetone. Attenuated total reflectance infrared (ATR-IR) spectra were recorded with an IFS 66/S FTIR spectrometer (Bruker) equipped with a Harrick Scientific
horizontal reflection Ge-attenuated total reflection accessory and the spectrum was collected for 64 scans. Raman spectroscopy and mapping (WiTec, Alpha 300 M) with an excitation wavelength of 532 nm were used to measure the crystallinity and binding with hydrogen.

Results and Discussion

Slow strain rate tests (SSRTs)

The stress–strain curve measured in the SSRT is shown (Fig. 1b). The behavior of charged bare copper is distinctly different, but that of graphene-coated copper is similar to that of uncharged bare copper. Under hydrogen charging, all of mechanical properties of graphene-coated copper are higher than those of bare copper. Detailed results of SSRT, such as time to fracture, ductility and ultimate tensile strength, are presented (Table S1). The strain at failure is used for assessing the HE resistance, and is presented (Fig. 1c). It was clearly declined as a result of the adverse effect of the hydrogen accumulated inside the metal. The fracture strain of the hydrogen-charged copper (45.5%) decreased compared to that of uncharged copper (50.6%). However, the fracture strain of hydrogen-charged graphene-coated copper (49.1%) is similar to that of uncharged copper. In the study of graphene fracture, monolayer graphene can be elongated at the strain of 25% until fracture [31]. From these results, it is supposed that hydrogen permeation can be effectively blocked by graphene coating until the strain of 25%. After that the cracked graphene coating reduces the surface area of underlying copper exposed to hydrogen, which may decrease the amount of hydrogen entering. Therefore, the strain at fracture of graphene-coated copper is slightly lower than that of uncharged bare copper.

In order to quantitatively evaluate the susceptibility of a specimen to the HE, the hydrogen embrittlement ratio (HER, %) is calculated by the following Eq. (1) [32]:

\[
\text{Hydrogen embrittlement ratio (HER, %) = } \left( \frac{\varepsilon_0 - \varepsilon_f}{\varepsilon_0} \right) \times 100
\]

![Image](image_url)

Fig. 1 – The results of specimen by slow strain rate tests. (a) schematic of hydrogen embrittlement test equipment is presented and it is composed of (1) a saturated calomel reference electrode, (2) a graphite counter electrode, (3) cylindrical tensile specimens (with a diameter of 6.35 mm and a gauge length of 25.4 mm), (4) an SSRT extending specimen, and (5) a corrosion cell containing an electrolyte. (b) the strain-stress curves (c) the strain (%) at failure and (d) hydrogen embrittlement ratio (HER, %).
where \( \varepsilon_o \) is the strain of the uncharged specimen at failure, and \( \varepsilon_H \) is the strain of the hydrogen-charged specimen at failure. The hydrogen embrittlement ratio (HER) is presented (Fig. 1d), where a higher HER signifies higher susceptibility of the metal to HE. The HER of hydrogen-charged graphene-coated copper (3.0\%) is much lower than that of hydrogen-charged copper (10.1\%). In other words, the susceptibility of copper to HE is reduced by using graphene coating. Meanwhile, fracture type of all specimens is not brittle. Due to the low diffusivity of hydrogen in face-centered cubic (FCC) crystal structure, hydrogen can be only trapped near the charging surface in case of room temperature charging [33]. Therefore, fracture type of copper is not changed from ductile to brittle until HER of 30\% due to the low susceptibility of copper to HE [32]. However, it is obvious that the susceptibility of copper is distinctly declined due to the graphene barrier. The results of fracture strain and HER confirm that graphene acts as an excellent hydrogen permeation barrier under tensile stress.

**Hydrogen content measurement**

The actual protective efficiency of graphene for hydrogen permeation is evaluated by measuring the amount of hydrogen inside of the specimen. Hydrogen is electrochemically charged for 12 h, and then the amount of hydrogen accumulated in the specimen is measured by gas chromatography in the temperature range from 50 to 500 °C. The accumulated hydrogen is easily released by heat treatment, which is generally used for eliminating hydrogen from materials [34]. In a recent study on graphene as a hydrogen storage material, the hydrogen absorbed by the graphene was dehydrogenated in the temperature range from 200 to 500 °C [18,35].

The hydrogen content released with temperature is presented (Fig. 2a). In the whole temperature range, the hydrogen content of bare copper was higher than that of graphene-coated copper. The maximum peak of the hydrogen content appeared at temperatures of 200 and 450 °C, corresponding to the diffusional (reversibly) and trapped (irreversibly) hydrogen in the metal, respectively. The absorbed hydrogen diffuses toward the interior of the material and a portion of hydrogen was retained in various preferential locations. For example, the lattice defects (grain boundaries, vacancies, dislocations) and precipitates (carbide) provide a variety of trapping sites [36]. The diffusional hydrogen is easily released by relatively low thermal energy, but comparatively high thermal energy is required to release the trapped hydrogen from the material. Therefore, the diffusional hydrogen is released at relatively low temperature, but the trapped hydrogen can be evolved after the critical temperature reached. The total amount of hydrogen released from graphene-coated copper (0.25 μmol/g) was much lower than that from bare copper (0.59 μmol/g) (Fig. 2b). Unfortunately, the protective efficiency of the monolayer graphene is not perfect, but it is expected that the efficiency may be enhanced by multiple layers of graphene, or optimization of graphene growth. The results of hydrogen measurement confirm that graphene is a proper barrier for hydrogen penetration, and effectively declines the susceptibility of copper to HE.

**Cathodic polarization**

Hydrogen can be electrochemically generated during the cathodic reaction of corrosion, electroplating, and cathodic protection, which increase the potential risk of HE. Hydrogen is produced by cathodic reduction reactions of water and acid by reactions:

\[
\text{H}_2\text{O} + e^- \rightarrow \text{H} + \text{OH}^- \hspace{1cm} (2)
\]

\[
\text{H}^+ + e^- \rightarrow \text{H} \hspace{1cm} (3)
\]

Most of the hydrogen atoms are recombined as the molecular hydrogen (H\(_2\)), but a portion of atomic hydrogen can diffuse into the lattice and retained in the material. These reactions can be occurred below the equilibrium potential (\(E_{\text{H}_2}\)) given by the Nernst Equation [28,37]:

\[
E_{\text{H}_2}^\circ (\text{mV}_{\text{SHE}}) = -59 \text{ pH} - 29.5 \log P_{\text{H_2}} \hspace{1cm} (4)
\]

![Fig. 2](image-url) – Hydrogen is electrochemically charged for 12 h, and then the amount of hydrogen accumulated inside the specimen is measured by gas chromatography in the temperature range from 50 to 500 °C. (a) the released hydrogen content with temperature and (b) the total amount of hydrogen released.
At pH = 1, corresponding to the electrolyte pH in the present study, the hydrogen equilibrium potential is \( -59 \text{ mV}_{\text{SHE}} \) (\(-300 \text{ mV}_{\text{SCE}}\)) for a hydrogen partial pressure \( P_{\text{H}_2}\) of 1 atm. The amount of hydrogen (\( N \)) produced per second per unit area (\( \text{cm}^2 \)) is given by Faraday’s law:

\[
N = \frac{i_{\text{red,H}}}{F}
\]

where \( i_{\text{red,H}} \) is the current density induced by cathodic reduction reaction, \( i_{0,H} \) is the exchange current density (current density at equilibrium potential \( E_{\text{corr}} \)), \( \beta_{\text{red,H}} \) is the Tafel constant (slope of cathodic polarization curve), \( E \) is any potential lower than \( E_{\text{H}_2} \), and \( F \) is the Faraday constant (96487 Coulomb/mole). This equation indicates that hydrogen production at the specimen surface occurs at higher rates as the current density \( i_{\text{red,H}} \) increases and the potential (\( E \)) becomes progressively less than \( E_{\text{H}_2} \).

The measured cathodic polarization curve and the schematic cathodic reduction behavior in a deaerated acid solution (pH = 1) is shown (Fig. 3). Based on the cathodic polarization curves (Fig. 3b), the hydrogen reduction reaction dominated the cathodic reactions below the potential of \(-300 \text{ mV}_{\text{SCE}}\). In the whole potential range (Fig. 3a), the hydrogen production rate (current density) on graphene-coated copper is much lower than that on bare copper. In a recent study on graphene as a corrosion-inhibiting coating, it was reported that graphene acts primarily as an inhibitor of the cathodic reactions [25]. Also, it was revealed that a graphene monolayer forms a charge transfer barrier between the solution and the graphene monolayer on the copper surface, which suppresses the corrosion reaction [24]. The charge transfer resistance of specimen is evaluated by electrochemical impedance spectroscopy (Fig. S1 and Table S2). The charge transfer resistance of graphene-coated copper is much higher than that of bare copper. From these results, it is confirmed that graphene acts as a charge transfer barrier for the hydrogen evolution reaction. Therefore, the graphene coating can improve the resistance against HE.

**Characterization of graphene**

In a recent study on graphene as a hydrogen storage material, it was revealed that hydrogen is absorbed by graphene as C–H sp\(^3\) bonds, which enables the hydrogen storage [18–20]. As a hydrogen barrier, it may be proposed that graphene interrupts hydrogen permeation by the interaction with hydrogen (formation of C–H sp\(^3\) bonds). This proposed barrier mechanism of graphene was verified through the C–H stretching bands of ATR-IR spectra and the bands of Raman spectra. The IR spectra of the hydrogenated (hydrogen charged) graphene clearly show aliphatic C–H stretching bands in the region of 2850–2950 cm\(^{-1}\), but they disappear for the dehydrogenated graphene [18]. ATR-IR spectra of pristine graphene and hydrogen-charged graphene were shown (Fig. 4a). There was no C–H stretching band (region of 2750–3000 cm\(^{-1}\)) for pristine graphene, but it was distinctly appeared for hydrogen-charged graphene.

The pristine graphene synthesized on copper foil by chemical vapor deposition is predominantly single-layer graphene, which is confirmed by the ratio of the G band peak (1580 cm\(^{-1}\)) and the 2D band peak (2680 cm\(^{-1}\)) in Fig. 4b. The D peak represents the disorder in the graphene and the D’ peak occurs due to the presence of defects in the graphene [38–40]. The D peak (1350 cm\(^{-1}\)), D’ peak (1620 cm\(^{-1}\)), and a combination mode of these peaks (D + D’ lie at 2950 cm\(^{-1}\)) appeared for hydrogen-charged graphene. When hydrogen absorbed onto graphene, geometrical deformation of the hexagonal structure was induced, which increase disorders and defects in the graphene [38,41]. During hydrogen charging, most of the hydrogen exists as a molecule and is physisorbed above the graphene. However, a portion of the hydrogen is retained as atomic hydrogen, and absorbed hydrogen on top of the graphene breaks π bonds and produces additional σ bonds, which induces transition from C=C to C–H and C–C bonds by forming sp\(^3\) hybridization bonds [41–43]. In order to understand why the atomic hydrogen breaks π bonds on the graphene sheet and produces additional σ bonds, we simply calculated the bonding energy (BE) by comparing which is more stable between graphene and hydrogenated graphene.
For the simple comparison, graphene was assumed that the hexagonal system consists of three C–C bonds (σ bond, BE 3.596 eV) and three C=C bonds (σ bond and π bond, BE 6.239 eV). The BE of hydrogenated graphene system consists of six C–C bonds and three C–H bonds (BE 4.280 eV) [44]. The change of free energy is calculated by:

$$
\Delta G = \sum \text{BE(graphene)} - \sum \text{BE(hydrogenated – graphene)} 
$$

$$
\Delta G = (3 \times 3.596 + 3 \times 6.239) - (6 \times 3.596 + 3 \times 4.280) = -4.911 \text{ eV} 
$$

Based on this result, the hydrogenated graphene is energetically favorable and thus atomic hydrogen can be chemically absorbed on graphene. Recent studies on adsorption of hydrogen onto graphene have reported that absorbed hydrogen forms hydrogen clusters [45,46] and cover graphene up to about 75% of surface [46,47]. The energy barrier depending on reaction process (penetration through graphene or absorption on graphene) is schematically shown (Fig. 4c). Passing through a center of hexagonal structure in graphene, above 2.89 eV is required because there is a repulsive force induced by strong electron cloud of graphene [48,49]. It is much larger than the energy barrier of C–H forming (0.18 eV) [50]. Hence, hydrogen penetration through graphene is much harder than C–H sp³ formation. From these experimental results and theoretical calculation, it can be proposed that the charged hydrogen is combined with graphene as C–H bonds, which interrupts the hydrogen penetration into copper.

**Conclusion**

In this study, the applicability of graphene as a protective barrier against HE was verified. To simulate the hydrogen embrittlement (HE), complex condition of tensile stress with simultaneous hydrogen charging was applied. The susceptibility of copper to HE is drastically depleted due to graphene protective coating, but protection effect was disappeared after graphene have been strained above 25%. The actual protective efficiency of graphene for hydrogen permeation is evaluated by measuring the amount of hydrogen inside of the specimen. The hydrogen permeation is sufficiently suppressed, but not perfect due to the defects of graphene. Through the characterization of hydrogen absorbed graphene, it was identified that graphene can effectively protect the hydrogen penetration by formation of C–H bonds.
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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.ijhydene.2014.05.132.

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