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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.

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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

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electrochemical discharge [15] and electrical field [16]. Development of new method, which can fundamentally protect material from hydrogen permeation, is still required.

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 °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 hydrogen evolution reaction on the specimen surface was investigated by cathodic polarization tests. Lastly, a protective mechanism of graphene against HE is proposed and verified by attenuated total reflectance infrared spectroscopy (ATR-IR) and Raman spectroscopy.

Material and methods

Graphene preparation

For the synthesis of graphene by chemical vapor deposition (CVD), copper foil (70 μm , purity 99.9%) was placed into a quartz tube. The specimen was annealed at 1050 °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_2O_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 $-1.0 \text{ mA}/\text{cm}^2$ for 12 h. A solution of 0.5 M sulfuric acid (H_2SO_4) + 250 mg/L arsenic trioxide (As_2O_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 $1.0 \times 10^{-6}/\text{s}$. 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_2O_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 mV_{SCE} from +50 mV_{OCP} to $-1200 \text{ mV}_{\text{SCE}}$.

Characterization of graphene

The hydrogen charged and uncharged graphene was transferred onto Si wafer ($\text{SiO}_2(300 \text{ nm})/\text{Si}$) 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

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