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The role of hydrogen in hardening/softening steel: Influence of the charging process

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ABSTRACT

Thermal desorption spectroscopy and nanoindentation techniques were employed to elucidate the key differences in the hydrogen (H) charging methods (electrochemical versus gaseous) and their consequences on the mechanical response of a low carbon steel. While electrochemical charging enhances the hardness, gaseous charging reduces it. This contrasting behavior is rationalized in terms of the dependency of the strength on the absorbed amount of H during charging and the H concentration gradient in the specimen.

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The chemical, physical, and mechanical aspects of metalhydrogen systems are widely researched in view of their importance in storage, transportation, and purification arenas [1–3]. In this context, one of the important - but often overlooked- aspects in laboratory scale studies is the influence of charging method on how H affects the properties of metals and alloys. The charging of H into a material is done either through electrochemical (also electrolytic or cathodic) route or through gaseous (also gas-phase or thermal) charging [4]. The former is performed in either an acid or an alkali solution under either galvanostatic or potentiostatic condition at room temperature (RT) [4], while the latter is conducted under a highly pressurized H₂ gas environment at temperatures that are usually higher than RT [5,6]. Although both methods have been widely used, only a limited literature, as to how these two methods differ, is available. Brass and Chêne [7] observed that electrochemical (E) charging can produce higher equivalent H₂ pressure, as compared to typical gaseous (G) charging, leading to higher H content in the material after charging. This is possibly the reason for surface damage (like blisters or cracks) that is observed more often in E-charged samples than in

* Corresponding authors. E-mail addresses: jinyoo@kist.re.kr (J.-Y. Suh), jijang@hanyang.ac.kr (J.-i. Jang). G-charged ones [4]. Additionally, theoretical calculations proposed that E-charging may induce more inhomogeneous H distribution in the sample than G-charging since the charging temperature, and thus H diffusivity, in the former are lower [7,8]. In this context, an important question that remains unanswered is the following; "can the change in charging methods bring any difference in the mechanical behavior?" A detailed understanding of this issue is crucial because the H-induced degradation in the mechanical performance (that is observed in almost all metals and alloys to be used for H storage and transportation) can restrict the use of H energy [2,9–11]. We address this question in this paper through a direct experimental comparison of the mechanical properties (measured using nanoindentation) and desorption behavior (evaluated using thermal desorption spectroscopy, TDS) of E- and G-charged low-carbon steel samples.

The composition (in wt.%) of the steel used in this study is Fe-0.07C-1.2Mn-0.15Si, and has a two-phase microstructure consisting of ferrite and pearlite, with the ferritic grain size and volume fraction of ~14.7 μ m and ~90%, respectively [12]. E-charging was performed at RT using a potentiostat/galvanostat equipment (HA-151A, Hokuto Denko, Tokyo, Japan) in 1 N H₂SO₄ solution including 0.25 g/l As₂O₃ (for avoiding H atom's recombination) for 3 h under a constant current density of 10 mA/cm².







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G-charging was performed in a Sieverts apparatus at 85 °C under constant pressure of 10 MPa, which is the maximum capacity of the apparatus, of gaseous H₂ for 96 h. The H desorption behavior of the charged samples was studied by a TDS equipped with a quadrupole mass spectrometer (QMS) (EX0014, R-DEC Company, Tsukuba, Japan). Immediately after charging, the samples were immersed in liquid nitrogen until TDS measurements. During TDS, hydrogenated samples were put into a vacuum glass tube and heated at a constant rate of 5 °C/min. The H₂ gas flow that desorbs from the specimen is recorded by QMS which allows for an accuracy of 0.01 weight ppm (wppm).

Nanoindentation tests were carried out using Nanoindenter-XP (formerly MTS; now Agilent Technologies, Oak Ridge, TN, USA) with a Berkovich indenter at a peak load of 25 mN and at constant indentation strain rates of (dh/dt)/h = 0.005, 0.025 and 0.1 s⁻¹. Before indentation, the specimen surface was mechanically polished with fine SiC paper (grit number up to 2000) and 0.3 um alumina to a mirror finish. Since some level of H out-gassing during surface preparation is inevitable [13], tests were started within 1800 s after charging, as per the procedures followed in prior studies [14-16], in order to minimize the influence of the possible out-gassing. Nanoindentation hardness values were calculated in accordance with Oliver and Pharr method [17]. Subsequent to indentation, the samples were etched in 3% nital acid, and surface observations were performed with an optical microscopy (Olympus, Tokyo, Japan) to determine the indent location, i.e., either ferrite grain interior (GI) or grain boundary (GB) regions.

The nanohardness variations with strain rate (from tests at GI and GB of E- and G-charged samples) are summarized in Figure 1. In all cases, increasing the strain rate leads to higher hardness. At a given strain rate, E-charging was found to enhance the hardness whereas G-charging leads to softening; this is found to be true at both GI and GB locations. Prior efforts for rationalizing



Figure 1. Variation in hardness values of (a) grain interior (GI) and (b) grain boundary (GB) as a function of indentation strain rate. Insets are representative OM images of indentation impressions located at GI and GB.

such H-induced hardening vs. softening in metals and alloys discuss various parameters that result in these opposing trends. They include internal parameters such as H concentration [18,19] and H trapping sites [20], and external parameters such as the stress state [14,21], pre-strain [22], temperature [10], and strain rate [10]. In the present study, most of the external parameters (temperature, stress, and pre-strain) are fixed and the fact that hardening or softening is seen at all strain rates suggests that the observed trend of hardening vs. softening is possibly a result of something internal to the material and how it interacts with the charged H.

To examine this further, TDS was performed on each sample and the resultant desorption curves are shown in Figure 2. In the TDS data of the uncharged sample (which is shown for comparison purposes), no peak was detected (except for some noise), supporting the effectiveness of the following TDS data of the charged samples. It is evident that the E-charged sample contains considerably more H (3.94 wppm) than the G-charged sample (0.24 wppm). It is reasonable to assume that in both the charging processes, H concentration at/near the sample surface reaches a maximum, which is determined by the charging conditions (galvanostatic or potentiostatic for E-charging, and H₂ pressure for G-charging; note that E-charging condition can be converted to "equivalent" H₂ pressure for comparison purposes) under an assumption that the surface kinetics are faster than the bulk diffusion rate. Subsequent to the surface saturation, H penetrates further into the sample until the whole sample attains the same concentration. After that, the rate of entry of H becomes zero as the sample gets saturated with H [23]. Therefore, higher H content of E-charging in Figure 2 seems reasonable in view of the method's easiness to provide a higher driving force for H absorption into material, i.e., higher equivalent H₂ pressure (that may not be reached in common lab-scale G-charging due to the issues of apparatus capacity or safety considerations [7])

In TDS curves, each H desorption peak represents the H desorption from different trapping sites. If the peak occurs at a higher temperature, it means that the H-trapping sites bind H in a stronger manner and hence require higher temperature so as to release the trapped H. Both the TDS scans obtained on E- and G-charged samples exhibit two peaks, that too in a similar temperature range. While the peak observed at a lower temperature corresponds to the relatively weak trapping sites (i.e., GBs and dislocations [24,25]), the second high temperature peak corresponds to relatively strong trapping sites with high binding energy with H. Considering the microstructure of the low-carbon steel (consisting of ferrite-pearlite phases with no major precipitates) examined in this work, possible strong trapping sites are the ferrite/cementite



Figure 2. TDS curves of electrochemically charged (E-charged), gas-phase charged (G-charged), and uncharged specimens. The curves for the G-charged and uncharged samples are also enlarged in the inset.

interfaces within the pearlite phase [26]. Note that ferritic steels, including the one examined here, are known to allow negligible amount of H locating in the interstitial sites (i.e., the lattice spacing), which is unlike austenitic steels [27,28], so that most of weak trapping sites are crystalline defects such as dislocations and GBs [24,25]. From Figure 2, it is reasonable to conclude that the charging method itself does not lead to any significant difference in the type of H trapping sites, but only in the H amount. As H always first occupies the strong trapping sites and only excessive H goes to weaker sites, it is reasonable to believe that in G-charging, not all but most H is trapped in the strong sites (corresponding to the second peak) while in E-charging the maximum amount of strongly trapped H is reached and the remaining H goes to the weak sites. It is also noteworthy in Figure 2 that both peaks for G-charging are shifted to a higher temperature regime (by \sim 60 °C) in comparison with those for E-charging. Because H prefers going to the strong sites first, the "average" binding energy for the small amount of H in G-charging may be higher than that of E-charging [29], which results in higher temperatures for the TDS peaks.

From the above observation, one may conclude that the difference in H concentration is the main reason for causing the opposite trends of hardness change observed in the two processes; i.e. higher H content in E-charged sample induces hardening while much lower H content in G-charged sample causes softening. This dependence of softening–hardening transition on H concentration can be explained based on the previous reports [18,19]. Small amount of H is known to enhance the mobility of screw dislocation by reducing the Peierls potential [18] or by nucleating double kink [19], leading to the observation of H-induced softening. With increasing H content, segregation of it to dislocations. These, in turn, pin the dislocations and hence increase the stress required for plastic deformation, resulting in H-induced hardening [19,29].

We did not observe a significant difference between GB and GI in terms of the variations in H-induced hardness (Fig. 1). This is possibly because the H binding energies at the GBs and at the dislocations of GI are similar. In addition, the plastic zone of the indentation made at GB includes the non-negligible portion of GI. Therefore, the hardness is not sensitive enough to decouple the GB effects as far as this study is concerned.

An important issue that remains unresolved is whether or not significant gradient in H distribution exists in the E-charged samples that have high H contents. To gain insights into this, additional TDS measurements were performed on E-charged samples. Immediately after E-charging, the charged side of the sample was ground such that only half of the sample is left at the end of



Figure 3. TDS curves of a typical E-charged specimen and a half piece specimen of which charging surface side was ground off right after E-charging.

grinding (see the inset of Fig. 3). Then, TDS spectrum was obtained again and compared with that of whole piece sample, as shown in Figure 3. The H concentration is much smaller in the half piece sample than in whole piece sample, implying that, in the E-charged sample, there indeed is a H concentration gradient from the charged surface. The first peaks in Figure 3 are significantly different in the two cases while the second peaks are almost the same. This suggests that H prefers to be trapped at the strong sites first, and only weakly trapped H (corresponding to the first peak) is contributing to the gradient. It is also an evidence for the possibility that the amount of the strongly trapped H reaches its equilibrium value at the used charging condition. Therefore, the H concentration gradient along the sample thickness is related with the higher fraction of weakly trapped H near the charged surface. Note that slightly higher second peak of half piece sample than that of whole piece sample (Fig. 3) is in agreement with previous observation that with reducing sample thickness (and thus diffusion distance), the desorption peak becomes higher and sharper [30].

Further support for the above hypothesis on the gradient in H concentration is obtained by cross-sectional nanoindentation. After E-charging, the sample was cut through thickness and nanoindentations at the intermediate rate of 0.025 s^{-1} were performed at the cross-sectional area, as illustrated in Figure 4a. The hardness variations, plotted as a function of the distance from the charged surface in Figure 4b, show a gradual reduction at both GI and GB. Except for the charged surface, the hardness values of cross-sectional area in the E-charged sample are always lower than those of the uncharged sample, indicating the H concentration in these locations is low enough to cause softening.

In contrast to the significant gradient observed in the E-charged sample, relatively small or no gradient is expected in G-charged sample due to homogeneous H distribution caused by relatively high charging temperature and long charging time. A simple theoretical calculation can be made to support it as follows. Assuming that lattice diffusion controls the H absorption during the charging of a plane sheet specimen from both sides of surfaces, the concentration of H at a given location having a distance (from surface) *x* at time *t* can be calculated as [3,31]:

$$C = C_{\rm S} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{C_{\rm S} \cos n\pi - C_{\rm S}}{n} \sin \frac{n\pi x}{l} \exp\left(\frac{-Dn^2 \pi^2 t}{l^2}\right) \tag{1}$$



Figure 4. Influence of non-uniform distribution of hydrogen along the thickness direction. (a) Cross-sectional micrographs showing four different locations where nanoindentations were made. (b) The through-thickness hardness profile where (1), (2), (3), and (4) indicate the locations defined in (a).

where l is specimen thickness, D is H diffusivity that is $1.05 \times 10^{-8} \text{ m}^2/\text{s}$ for α -Fe at 85 °C (the slowest possible value according to Ref. [32]), C_s is the H concentration on the specimen surface and can be determined by Sieverts' law, $C_S = K \cdot p^{0.5}$ [3,33], where K is solubility constant (=3.90 \times 10⁻¹⁰ wppm/Pa^{0.5} [9]) and p is the applied H₂ pressure (=10 MPa in this study). The calculation according to Eq. (1) shows that the H in the lattice will reach equilibrium content (= 1.23×10^{-6} wppm) in a whole body of the specimen in G-charging for ~ 10 min, leading us to conclude that G-charging time in this study, 4 days, is long enough for obtaining homogeneous H distribution, even if we consider the slowdown of the diffusion due to the presence of crystalline defects such as dislocations. GBs. and phase interfaces. Note that there is some difficulty in applying the above calculation to E-charging case due to the undefined relation between H concentration and current density with common units (which was previously proposed for electrochemical H permeation tests [34,35], but not directly applicable to E-charging).

In summary, the different mechanical behavior of E- and G-charged low-carbon steel samples was systematically investigated through nanoindentation and TDS experiments. Contrary H-induced nanohardness changes, i.e. hardening by E-charging while softening by G-charging, were observed. The results indicate that the hardening/softening behavior is H-content-dependent, i.e. relatively higher H content by E-charging causes hardening while lower H content by G-charging induces softening. It is also revealed that, unlike the uniform distribution of H in G-charged sample, E-charging induces H concentration gradient through the thickness and this gradient is associated only with the weakly trapped H.

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References

[1] L. Schlapbach, A. Züttel, Nature 414 (2001) 353.

- [2] J.-A. Lee, D.-H. Lee, M.-Y. Seok, U.B. Baek, Y.-H. Lee, S.H. Nahm, J.-I. Jang, Mater. Charact. 82 (2013) 17.
- [3] Y.-I. Wang, J.-Y. Suh, Y.-S. Lee, J.-H. Shim, E. Fleury, Y.W. Cho, S.-U. Koh, J. Membr. Sci. 436 (2013) 195.
- [4] K. Verbeken, in: R.P. Gangloff, B.P. Somerday (Eds.), Gaseous Hydrogen Embrittlement of Materials in Energy Technologies, Woodhead Publishing, Cambridge, 2012, pp. 31–33.
- [5] C. San Marchi, B.P. Somerday, S.L. Robinson, Int. J. Hydrogen Energy 32 (2007) 100.
- [6] Y. Mine, Z. Horita, Y. Murakami, Acta Mater. 58 (2010) 649.
- [7] A.-M. Brass, J. Chêne, Corros. Sci. 48 (2006) 3222.
- [8] U. Hadam, T. Zakroczymski, Int. J. Hydrogen Energy 34 (2009) 2449.
- [9] J.P. Hirth, Metall. Trans. A 11A (1980) 861.
- [10] H.K. Birnbaum, P. Sofronis, Mater. Sci. Eng. A 176 (1994) 191.
- [11] D.K. Han, Y.M. Kim, H.N. Han, H.K.D.H. Bhadeshia, D.-W. Suh, Scr. Mater. 80 (2014) 9.
- [12] M.-Y. Seok, Y.-J. Kim, I.-C. Choi, Y. Zhao, J.-I. Jang, Int. J. Plast. 59 (2014) 108.
- [13] O. Takakuwa, Y. Mano, H. Soyama, Int. J. Hydrogen Energy 39 (2014) 6095.
- [14] D.-H. Lee, J.-A. Lee, M.-Y. Seok, U.B. Baek, S.H. Nahm, J.-I. Jang, Int. J. Hydrogen Energy 39 (2014) 1897.
- [15] D.F. Bahr, K.A. Nibur, K.R. Morasch, D.P. Field, JOM 55 (2003) 47.
- [16] A. Shibata, H. Takahashi, N. Tsuji, ISIJ Int. 52 (2012) 208.
- [17] W.C. Oliver, G.M. Pharr, J. Mater. Res. 7 (1992) 1564.
- [18] H. Matsui, H. Kimura, A. Kimura, Mater. Sci. Eng. 40 (1979) 227.
- [19] R. Kirchheim, Scr. Mater. 67 (2012) 767.
- [20] Y. Zhao, I.-C. Choi, M.-Y. Seok, U. Ramamurty, J.-Y. Suh, J.-I. Jang, Scr. Mater. 93 (2014) 56.
- [21] R. Miresmaeili, L. Liu, H. Kanayama, Int. J. Press. Vessels Pip. 99–100 (2012) 34.
- [22] E. Tal-Gutelmacher, D. Eliezer, T. Boellinghaus, J. Alloys Compd. 440 (2007) 204.
- [23] E. Protopopoff, P. Marcus, in: P. Marcus (Ed.), Corrosion Mechanisms in Theory and Practice, Taylor & Francis Group, Boca Raton, 2012.
- [24] D. Pérez Escobar, K. Verbeken, L. Duprez, M. Verhaege, Mater. Sci. Eng. A 551 (2012) 50.
- [25] W.Y. Choo, J.Y. Lee, Metall. Trans. A 13A (1982) 135.
- [26] J.S. Kim, Y.W. Lee, D.L. Lee, K.-T. Park, C.S. Lee, Mater. Sci. Eng. A 505 (2009) 105.
- [27] S. Pillot, L. Coudreuse, in: R.P. Gangloff, B.P. Somerday (Eds.), Gaseous Hydrogen Embrittlement of Materials in Energy Technologies, Woodhead Publishing, Cambridge, 2012, pp. 55–57.
- [28] W.Y. Choo, J.Y. Lee, J. Mater. Sci. 16 (1981) 1285.
- [29] A. Barnoush, M. Asgari, R. Johnsen, Scr. Mater. 66 (2012) 414.
- [30] S.-M. Lee, J.-Y. Lee, Metall. Trans. A 17A (1986) 181.
- [31] J. Crank, The Mathematics of Diffusion, second ed., Oxford University Press, London, 1975.
- [32] K. Kiuchi, R.B. McLellan, Acta Metall. 31 (1983) 961.
- [33] Y. Zhao, I.-C. Choi, M.-Y. Seok, M.-H. Kim, D.-H. Kim, U. Ramamurty, J.-Y. Suh, J.-I. Jang, Acta Mater. 78 (2014) 213.
- [34] W. Beck, J.O'M. Bockris, J. McBreen, L. Nanis, Proc. R. Soc. London A 290 (1966) 220.
- [35] E.G. Dafft, K. Bohnenkamp, H.J. Engell, Corros. Sci. 19 (1978) 591.