Nondestructive observation on tensile property change of hydrogen-exposed Cr-Mo-V steel HAZ using an instrumented indentation technique

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Long-term service of materials in environments of high hydrogen pressure can cause various sorts of damage such as temper embrittlement, hydrogen-assisted degradation and hydrogen attack [1–3]. The demand in the petrochemical refinery industry for superior resistance to this damage has promoted the use of V-modified Cr-Mo steels for petrochemical reactor vessels.

Like other structural steels, the Cr-Mo-V steels undergo welding during vessel construction. The superior properties of this steel must be carefully reconsidered because, as is well accepted, welding can seriously alter metallurgical and mechanical properties, generally for the worse. In particular, the coarse-grained heat-affected zone (CGHAZ) adjacent to the fusion line is known as one of the weakest regions in the welded joints [4]. In addition, it has been reported that the CGHAZs of Cr-Mo steels are much more sensitive to hydrogen-induced damage than the base material [2]. Therefore, proper evaluation of the time-dependent change in mechanical properties of Cr-Mo-V steel joint CGHAZs exposed to hydrogen is very important in assessing the safety performance of the petrochemical reactor vessels under high hydrogen pressure. The present work, the first of a series of studies of the time-dependent degradation of CGHAZs in Cr-Mo-V steels according to increasing hydrogen exposure time, uses a nondestructive instrumented indentation technique to clarify the change in tensile properties.

Since complex microstructural gradients exist within the HAZ, weld simulations were made in a systematic investigation of the tensile properties of the small target region, i.e. CGHAZ. Commercial-grade 2.25Cr-1Mo-V steels, of chemical composition 0.15C-0.09Si-0.45Mn-0.006P-0.001S-0.12Ni-2.4Cr-0.98Mo-0.29V, were thermally cycled in a Thermicmaster system to simulate the CGHAZ. After reaching 1623 K, the specimens were held for 3 s and cooled down from 1073 K to 773 K with constant cooling time of 60 s. The cooling rate was approximately equivalent to that in tandem submerged arc welding (SAW) with heat input 27 kJ/cm in a 25-mm-thick plate. The simulated CGHAZ specimens experienced post-weld heat treatment at 963 K for 24 h, and then were exposed at 873 K to a hydrogen pressure of 54 MPa for 408 and 1000 h.

Conventional tensile tests need specimens of a particular size and thus cannot easily be applied to testing local regions such as simulated CGHAZ specimens. To overcome these limitations, an instrumented indentation technique was applied in this study using Advanced Indentation System-2000^{TM} (Frontics, Inc., Seoul, Korea), with spherical WC indenter of radius 0.5 mm.

The flow curve showing the relationship between true stress and true strain was obtained according to the following analysis. Fig. 1a is a schematic diagram of a typical indentation load-depth curve measured in instrumented indentation tests. The representative stress and strain were defined in terms of the measured indentation contact parameters such as contact depth (h_c), indenter shape and the morphology of the deformed sample surface. Real contact properties were determined by considering both elastic deflection and plastic material pile-up around the spherical indenter, as shown in Fig. 1b.

The contact depth at maximum indentation load can be evaluated by analyzing the unloading curve with the concept of indenter geometry and elastic deflection [5]:

$$h_c = h_{\max} - \omega(h_{\max} - h_i) \tag{1}$$

where h_i is the intercept indentation depth (see Fig. 1a) and the indenter shape parameter ω is 0.75 for the spherical indenter. The material pile-up around the indentation makes the actual contact radius larger than expected. The extent of this pile-up can be determined by a constant c and the steel work-hardening exponent n in Equation 2 [6, 7]:

$$c^2 = \frac{a^2}{a^{*2}} = \frac{5(2-n)}{2(4+n)} \tag{2}$$

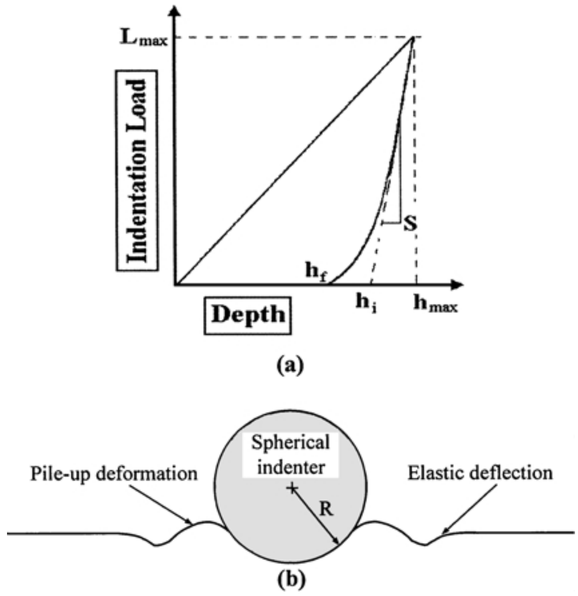


Figure 1 Schematic diagrams of (a) typical indentation load-depth curve and (b) elastic and plastic deformation around indenter.

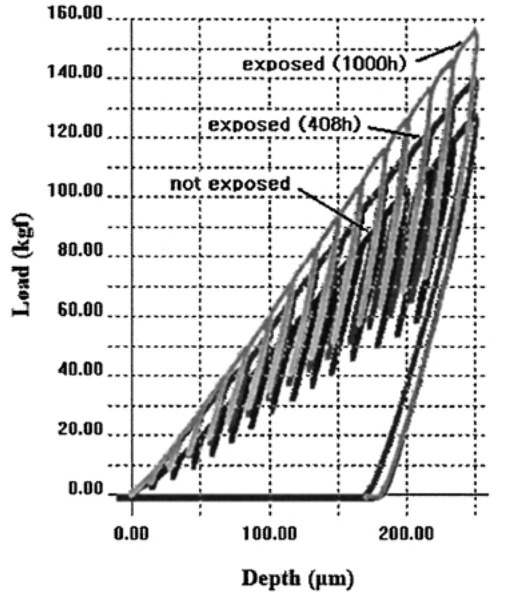


Figure 2 Indentation load-depth curves vs. hydrogen exposure time.

where a is the actual contact radius and a^* is the contact radius without the pile-up. Using the geometrical relationship of the spherical indenter, the real contact radius is expressed in terms of h_c and indenter radius R as:

$$a^2 = \frac{5(2-n)}{2(4+n)}\left(2Rh_c - h_c^2\right) \tag{3}$$

Using these parameters, the representative stress and strain were determined as follows. The representative strain of indentation ε_R is evaluated from the material displacement beneath the indenter along the indentation axis direction. The strain can be expressed as in Equation 4 at the contact radius position by multiplying a fitting constant α (taken as 0.1 for various steels [8]):

$$\varepsilon_R = \frac{\alpha}{\sqrt{1-(a/R)^2}}\frac{a}{R} \tag{4}$$

On the other hand, it is well known that three deformation steps occur during spherical indentation: the elastic, elastic/plastic and fully plastic stages. Since the elastic and elastic/plastic deformation steps generally occur at very low indentation load in steels, only the plastic deformation region was considered in this study. Using the mean contact pressure (P_m), obtained according to Equation 5 in terms of maximum load ($L_{\max}$) and contact area, the representative stress (σ_R) can be evaluated using the relationship with contact mean pressure in Equation 6 [9]:

$$P_m = \frac{L_{\max}}{\pi a^2} \tag{5}$$

$$\frac{P_m}{\sigma_R} = \Psi \tag{6}$$

where Ψ is a constraint factor for plastic deformation with upper limit about 3 for fully plastic deformation of steels. The exact values of the work-hardening index, representative stress and strain are calculated by the iteration method [8]. In this study, cyclic indentation tests with 15 loading/unloading sequences were made at 0.3 mm/min on each sample. Representative stress and strain values were determined by analyzing each unloading curve according to the above procedure, and then the values were fitted as a simple power-law-type Hollomon Equation 7:

$$\sigma = K(\varepsilon)^n \tag{7}$$

where K is the strength coefficient. While true stress always increases with true strain, the ultimate tensile strength was determined using Consiére's criterion [10].

Figs 2 and 3 show the indentation load-depth curves obtained from the instrumented indentation tests on the

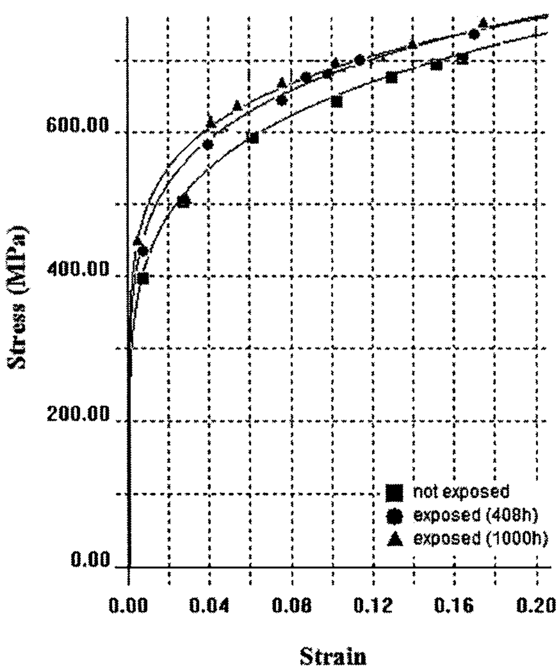
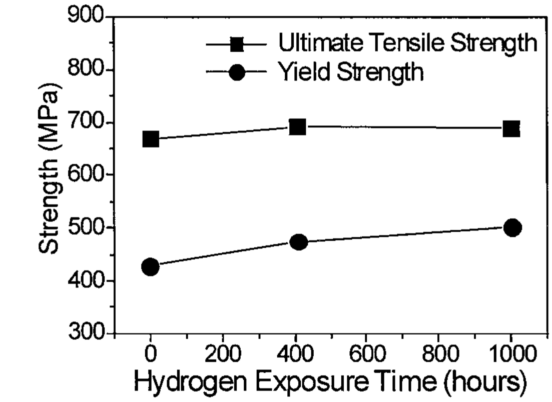
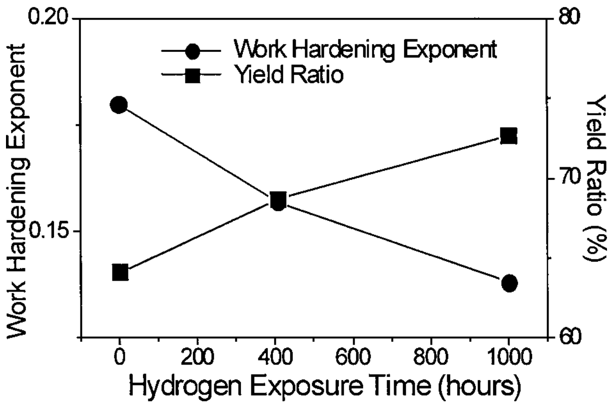


Figure 3 Change in plastic flow from instrumented indentation tests with hydrogen exposure time.



(a)



(b)

Figure 4 Variations in tensile properties with increasing hydrogen exposure time: (a) yield and ultimate tensile strengths; (b) work-hardening exponent and yield ratio.

simulated CGHAZ specimens and the true stress-strain curves analyzed from the multiple load-depth curves. As shown in Fig. 2, the indentation load increased with increasing hydrogen exposure time at a given maximum indentation depth, 250 μm. The true stress-true strain curves in Fig. 3 indicate a trend similar to the load-depth curves.

From the flow curves, the changes in tensile properties were investigated individually in detail as shown in Fig. 4. The variations in yield strength and ultimate tensile strength with hydrogen exposure time appear in Fig. 4a. While yield strength increased with increasing hydrogen exposure time, the variation in ultimate tensile strength is almost negligible and there is no apparent dependence on hydrogen exposure time. From these results it can be seen that there is no significant strength degradation such as softening, as generally observed in other high-temperature structural steels.

However, it is risky to assess hydrogen-assisted degradation on the basis of strength variations alone, because degraded materials generally show changes not only in strength-related properties such as softening but also in fracture-related properties, i.e. embrittlement. Evaluation of the extent of embrittlement is also of great interest to prohibit possible brittle fracture during plant operation. With this in mind, the authors looked for other degradation parameters that can be obtained from nondestructive indentation tests and can indicate the degree of embrittlement. Fig. 4b shows the variations in work-hardening exponent and yield-strength-to-tensile-strength ratio. The work-hardening exponent is a measure of the uniform elongation of the tested material and thus directly related to its deformability. Thus its value can give useful information on embrittlement, while strength and hardness can give only limited information about softening or hardening. In Fig. 4b, a considerable reduction in the exponent (about 20%) was identified, meaning that the material had become embrittled by hydrogen attack (perhaps by the formation of methane bubbles at grain boundaries [11]). Especially in structural materials like this Cr-Mo-V steel, the change in exponent value must be estimated carefully, since there are possible increases in local deformation concentration and decreases in strain-absorption ability of the structure with increasing exponent value.

Fig. 4b also shows the variation in yield-strength-to-tensile-strength ratio, the so-called yield ratio (YR), as another degradation measure indicating the degree of embrittlement. The value of YR increases with increasing hydrogen exposure time, implying increased embrittlement due to hydrogen attack. The change in YR is known to be inversely proportional to work-hardening exponent variation [12]. The greatest advantage of using YR instead of the work-hardening exponent is its wide applicability to industrial structures. Generally the work-hardening exponent is not used in industrial specifications for new structural materials, and thus work-hardening exponent values of degraded materials cannot be easily compared with those of new materials. But the yield and tensile strengths, which are all that is needed for determining YR, are generally specified and recorded for new materials. Thus the YR values of degraded materials can be used to assess embrittlement by comparison to the values for new materials.

In present work, we have seen that (1) the tensile properties of small regions simulating CGHAZ in 2.25Cr-1Mo-V steel were measured quantitatively and nondestructively by an instrumented indentation technique with a spherical indenter, (2) the main degradation of the CGHAZ in 2.25Cr-1Mo-V steel with increasing hydrogen exposure time is not softening but embrittlement, and (3) the extent of embrittlement can be evaluated using parameters such as the work-hardening exponent and yield ratio, which can be obtained from the non-destructive indentation tests. The authors plan to make a microstructural analysis of the tensile property change with hydrogen exposure time.

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