Influence of Specimen Thickness on Thermal Desorption Spectrum of Hydrogen in High Strength SCM435 Steel

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Thermal desorption analysis (TDA) of hydrogen was carried out in high strength SCM435 steel in which the strain field of dislocation presumably is a major hydrogen trap site. Cylindrical specimens of radius 0.5–5 mm were cathodically charged until saturated and were heated at a rate ranging from 25 to 200°C/hr, aiming to vary the condition of hydrogen desorption from detrapping- to diffusion-control. For specimens of radius 0.5 mm the trap energy of hydrogen evaluated from the Choo-Lee (C-L) plot was as high as 33.8 kJ/mol, while for thicker specimens it was significantly smaller, i.e. 25.6–27.5 kJ/mol. The possible causes for the dependence of the trap energy on specimen thickness are discussed in terms of the influence of initial hydrogen distribution on the peak temperature and the deviation from local equilibrium of hydrogen during desorption. If pre-exposure is carried out for a sufficiently long time prior to TDA, the C-L plot seems to give a correct detrap energy even in the mixed-control desorption.

KEY WORDS: hydrogen; thermal desorption analysis; local equilibrium; high strength low alloy steel; detrapping-control; diffusion-control.

1. Introduction

Thermal desorption analysis (TDA) is widely used to identify the trap site and the state of presence of hydrogen in steel.1) In a previous study we developed a finite difference computer program which simulates the spectrum of thermal desorption analysis (TDA) of hydrogen in steel.2) The simulation model was based upon the McNabb-Foster model3) with the hydrogen trap sites of discrete binding energies. The key parameters, e.g. trap energy and detrapping coefficient, were determined by fitting with the spectra of cylindrical specimens of 2.5 mm in radius by trial and error. From the value of the detrapping coefficient $p_0=25–30$ s$^{-1}$,2) it was thought that hydrogen desorption seemed to occur almost in the detrapping-controlled condition because the interval of detrapping events, i.e. inverse of $p_0$, was calculated to be greater than the diffusion time to the surface of the specimen.

The TDA spectrum is highly dependent on the specimen thickness. In a thin specimen lattice diffusion of hydrogen does not play a significant role in desorption because detrapped hydrogen almost instantly diffuses to the surface of the specimen. On the other hand, in a thick specimen lattice diffusion has a major influence on the spectrum shape because hydrogen atoms can escape from the trap site to the strain field of dislocation presumably is a major hydrogen trap site. Cylindrical specimens of radius 0.5–5 mm were cathodically charged until saturated and were heated at a rate ranging from 25 to 200°C/hr, aiming to vary the condition of hydrogen desorption from detrapping- to diffusion-control. For specimens of radius 0.5 mm the trap energy of hydrogen evaluated from the Choo-Lee (C-L) plot was as high as 33.8 kJ/mol, while for thicker specimens it was significantly smaller, i.e. 25.6–27.5 kJ/mol. The possible causes for the dependence of the trap energy on specimen thickness are discussed in terms of the influence of initial hydrogen distribution on the peak temperature and the deviation from local equilibrium of hydrogen during desorption. If pre-exposure is carried out for a sufficiently long time prior to TDA, the C-L plot seems to give a correct detrap energy even in the mixed-control desorption.

2. Mixed-control Desorption

The previously developed finite difference code2) is used for simulation. The McNabb-Foster (M-F) theory consists of two equations. One is the diffusion equation with source (or sink) term expressed by,

$$\frac{\partial c}{\partial t} + N_t \frac{\partial \theta_t}{\partial t} = D_L \left( \frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} \right) \quad \text{(1)}$$

where $c$ is hydrogen concentration in the lattice, $N_t$ is the density of trap sites, $\theta_t$ is occupancy fraction at the trap site, $D_L$ = $5.8 \times 10^{-8}$ exp($-4.5 \times 10^7/RT$) m$^2$/s$^3$) is the lattice diffusivity of hydrogen, $r$ is the radial coordinate and $t$ is time. The other equation describes the rate of change of the occupancy fraction and is given by,

$$\frac{\partial \theta_t}{\partial t} = kct(1-\theta_t) - p\theta_t \quad \text{(2)}$$

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Here,
\[ k = k_0 \exp\left(\frac{-E_D}{RT}\right) \] .............................................. (3)
and,
\[ p = p_0 \exp\left(\frac{-E_B + E_D}{RT}\right) \] .............................................. (4)
are, respectively, trapping and detrapping coefficients, \( E_D \) (=4.5 kJ/mol) is the activation energy of lattice diffusion and \( E_B \) is the binding energy of hydrogen with the trap site. \( R \) is the gas constant and \( T \) is temperature. The pre-exponential factors \( k_0 \) and \( p_0 \) are related to each other as \( k_0 = p_0/N_L \) where \( N_L = (5.08 \times 10^{29} \text{ m}^{-3}) \) is the number of available sites of hydrogen in the lattice of bcc Fe. \( N_t \) was evaluated from the relationship \( N_t = Vp/a \), where \( V \) is the number of hydrogen occupation sites per Fe atom plane, \( a \) is the atom spacing (=2.49 \times 10^{-10} \text{ m}) and \( p \) is the dislocation density in the martensite lath, which was assumed to be 5 \times 10^{15} \text{ m}^{-2} \) in this study.\(^9\) Moreover, \( V \) was assumed to be 10, which implies that the effective radius of dislocation as a trap site is ~1 nm.\(^2\) At the start of simulation the specimen size is so large that the diffusion time is longer than the time interval of detrapping, the desorption is controlled by diffusion of hydrogen, and hydrogen desorption can be ignored, the desorption rate is equal to the rate of escape from the trap site. It is important to note that the concentration of hydrogen is uniform and in equilibrium between the lattice and the trap site, which often makes the initial evolution rate very high.

When the specimen size is so small that both re-trapping and diffusion of hydrogen can be ignored, the desorption rate is equal to the rate of escape from the trap site. It is well known that in this condition the detrap energy, denoted \( E_D \), can be evaluated from the slope of \( \ln(\phi/T_p^5) \) vs \( 1/T_p \) plot proposed by Choo-Lee (C-L),\(^4\) where \( T_p \) is peak temperature and \( \phi \) is ramp rate. On the other hand, when the specimen size is so large that the diffusion time is longer than the time interval of detrapping, the desorption is controlled by diffusion of hydrogen, and hydrogen desorption is described by the diffusion equation without a source or sink term using the so-called effective diffusivity.\(^11\) The C-L plot is also applicable to diffusion-controlled desorption if pre-exposure is carried out for a sufficiently long time,\(^5,6\) whereas, the \( \ln(\phi/T_p^5) \) vs \( 1/T_p \) plot, another formula of Kissinger-type desorption proposed by Lee and Lee,\(^12\) does not yield a correct value of detrapp energy.

In practice a C-L plot is often carried out without paying due attention to the condition of desorption. To the best of the author’s knowledge there has been no discussion as to the validity of C-L plot in desorption between these two extremes. One may be able to examine this issue experimentally by performing TDA using specimens of varying thickness. SCM435 steel seems to be appropriate for this purpose because the TDA spectrum of hydrogen is relatively simple and the proposed trap energies do not scatter widely in low alloy martensitic steels.\(^13\) Moreover, the M-F model can deal with the diffusion and trapping of hydrogen in any condition between detrapping- and diffusion-control without relying upon the local equilibrium assumption.\(^14\) In the model one can calculate the parameter defined by,
\[ R_{LE} = \frac{\theta_1}{\theta_{LE}} \] .............................................. (5)
to observe the degree of deviation from local equilibrium during desorption, where \( \theta_1 = c/N_L \) is the occupancy fraction of hydrogen in the lattice and \( \theta_{LE} \) is the value at equilibrium with the trap site given by,\(^11\)
\[ \theta_{LE} = \frac{\theta_1}{1 + \theta_1}\exp\left(-\frac{E_D}{RT}\right) \] .............................................. (6)
\( R_{LE} \) is close to zero in the detrapping-controlled condition in which hydrogen atoms that escaped from the trap site are released almost instantly from the specimen surface. On the contrary, \( R_{LE} \) is equal to unity in the diffusion-controlled desorption in which local equilibrium of hydrogen is maintained, i.e., \( \theta_1 = \theta_{LE} \), and thus, it increases from zero to unity with specimen thickness. It should also be noted that \( \theta_1, \theta_0, \theta_{LE} \) and \( R_{LE} \) are all functions of the radial coordinate \( r \). The amount of deviation from local equilibrium is thus dependent upon the position within the specimen.

### 3. Experimental Procedure

SCM435 is a high-strength medium carbon Cr–Mo steel. The alloy contained 0.35 mass%C, 0.22 mass%Si, 0.78 mass%Mn, 1.16 mass%Cr and 0.17 mass%Mo, as has been presented elsewhere.\(^2\) The alloy was machined into a cylinder of 0.5(R1), 1.25(R2), 2.5(R3), and 5 mm (R4) in radius (\( t_0 \)) and 100 mm in length, see Table 1. Specimens were austenitized at 950°C for 1 hr under Ar atmosphere and quenched into an oil bath maintained at 60°C. They were then tempered at 300°C for 1 hr under Ar and quenched into water. The microstructure was tempered lath martensite presumably with a small amount of retained austenite.\(^15\)

Specimens were cathodically charged with hydrogen at a current density of 0.2 mA/cm\(^2\) in a 3%NaCl aqueous solution with the addition of NH4SCN (3 g per litre) as a catalyst at ambient temperature. They were then kept in liquid nitrogen. TDA was carried out using gas-chromatograph at constant heating rates from 25 to 200°C/hr. Since the heating rate employed in TDA is slow, it is designated ramp rate hereafter. The amount of released hydrogen was measured at the interval of 5 min using Ar as a carrier gas, and the total amount of charged hydrogen was obtained from the accumulated hydrogen flux at the end of the analysis, assuming that charged hydrogen was all diffusible. The procedure of TDA has also been described elsewhere.\(^2\)

### 4. Results

#### 4.1. Cathodic Charge of Hydrogen

Figure 1(a) displays the TDA spectra of specimen R4 at various charging times, and in Fig. 1(b) the amount of charged hydrogen was plotted against charging time for all specimens.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>radius, mm</th>
<th>Charging time, h</th>
<th>Amount of hydrogen, ppm</th>
<th>Detrap energy ( E_D ), kJ/mol</th>
<th>Detrapping coefficient ( p_0 ), s(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>0.5</td>
<td>48</td>
<td>1.72</td>
<td>38.3</td>
<td>4 000</td>
</tr>
<tr>
<td>R2</td>
<td>1.25</td>
<td>96</td>
<td>3.84</td>
<td>31.9</td>
<td>50</td>
</tr>
<tr>
<td>R3</td>
<td>2.5</td>
<td>96</td>
<td>4.06</td>
<td>30.1</td>
<td>10</td>
</tr>
<tr>
<td>R4</td>
<td>5.0</td>
<td>96</td>
<td>4.39</td>
<td>32.0</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 1. Condition of hydrogen charge and detrapp energy deduced from Choo-Lee plot.
It seems that specimens of radius 1.25 mm or larger were saturated with hydrogen by charging for 96 h. Only one charging time (48 hr) was employed for R1. The amount of charged hydrogen is considerably less than those of the other specimens presumably because several specimens were charged simultaneously in an electrolysis cell.

Table 1 shows the charging time and the concentrations of charged hydrogen in the specimens used for TDA.

4.2. Variation of TDA Spectrum with Ramp Rate and Choo-Lee Plot

Figures 2(a) through 2(d) display TDA spectra of all specimens. It seems that specimens of radius 1.25 mm or larger were saturated with hydrogen by charging for 96 h. Only one charging time (48 hr) was employed for R1. The amount of charged hydrogen is considerably less than those of the other specimens presumably because several specimens were charged simultaneously in an electrolysis cell.
specimens at a ramp rate of $\phi=100^\circ$C/hr. At the lowest ramp rate ($\phi=25^\circ$C/hr) the hydrogen evolution rate continued to decrease in all specimens except specimen R4. The highest peak temperature ($T_p$) was 189$^\circ$C of R4 at $\phi=200^\circ$C/hr. The peaks became flatter and broader with specimen thickness. Since the amount of hydrogen released from the specimen was measured at a time interval of 5 minutes, the temperature interval increased significantly at a faster ramp rate, which may give rise to an error of $\pm 8.3^\circ$C in $T_p$ at $\phi=200^\circ$C/hr. In order to remedy this situation cubic spline interpolation was adopted for the determination of $T_p$ for thick specimens.

Figures 3(a) through 3(d) present the C-L plots for all specimens. As shown in Table 1, $E_d$ values determined from the slope are in good agreement with that assumed previously ($E_B=27$ kJ/mol), while that of R1 is significantly greater. The $p_0$ values were evaluated by fitting with the observed $T_p$'s for each specimen. They are also similar to or even smaller than the value previously determined ($p_0=30$ s$^{-1}$) except R1.

5. Discussion

5.1. Re-evaluation of $E_d$ and $p_0$

Assuming that the binding energy of hydrogen trap site is identical in all specimens, the peak temperatures are calculated in all specimens using the $E_d$ and $p_0$ values of specimen R3. Figure 4(a) shows clearly that they do not reproduce $T_p$'s of the other specimens. A small $p_0$ value implies that desorption occurred under detrapping-control and thus, $T_p$ depends weakly on specimen thickness. On the other hand, the $E_d$ and $p_0$ of R1 fit much better with $T_p$'s of the other specimens. By trial and error one can get an overall fit at $E_B=35$ kJ/mol and $p_0=5 \times 10^{3}$ s$^{-1}$ as displayed in Fig. 4(b). Although the agreement was worse, the best fit $E_d$ and $p_0$ values were similar for $\rho=10^{16}$ m$^{-2}$. These $E_B$ values are somewhat smaller than the trap energy of hydrogen at an edge dislocation in bcc Fe,$^{16,17)}$ presumably because the core of dislocation in lath martensite that formed upon quenching are occupied by carbon$^{10,18)}$ and thus the sites of a higher binding energy of dislocation are not available for hydrogen.

Figure 5 presents the Arrhenius plot of the Oriani’s effective diffusivity,$^{11)}$

$$D_{eff} = \frac{D_L}{1 + \frac{N_t}{N_B} \exp \left( \frac{E_B}{RT} \right)}$$

(7)

calculated with $E_B=35$ kJ/mol for three $\rho$ values. The intersection of two straight lines extrapolated from the low and high temperature parts, denoted $T_{eff}$, varies consider-
ably with Nt/NL and thus, dislocation density. D_{eff} begins to deviate from the straight line at a temperature significantly below T_{eff}.

Figures 2(a) through 2(d) include TDA spectra simulated using E_B=25.6 kJ/mol, and p_0=10 s^{-1}, and b) E_B=35 kJ/mol, and p_0=5 \times 10^3 s^{-1}. Open and solid symbols indicate peak temperatures of experimental and simulated peaks, respectively.

Fig. 4. Fitting with experimental peaks of all specimens with a single set of E_B and p_0 values. a) E_B=25.6 kJ/mol, and p_0=10 s^{-1}, and b) E_B=35 kJ/mol, and p_0=5 \times 10^3 s^{-1}. Open and solid symbols indicate peak temperatures of experimental and simulated peaks, respectively.

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Fig. 5. Arrhenius plot of effective diffusivity of hydrogen with varying dislocation density of lath martensite. D_L is the diffusion coefficient of hydrogen in αFe.

5.2. Comparison of Measured and Calculated Detrap Energies

In Fig. 7 E_d’s obtained from experimental and simulated peaks with E_B=33 (grey dashed line) and 35 kJ/mol experimental spectra. The variations of R_{LE} near the center (r/r_0=0.05) and the edge of a specimen (r/r_0=0.95) are presented in Figs. 6(a) and 6(b), respectively. The arrows indicate the temperature at which the hydrogen evolution rate fell to one hundredth of the peak evolution rate, i.e. the end temperature of the peak. Dotted lines indicate R_{LE} of specimens of radius 0.1 mm.

Fig. 6. Variation of R_{LE} parameter with temperature during TDA a) in the center, and b) near the edge of the specimen. Arrows indicate the temperature at which the hydrogen evolution rate fell to one hundredth of the peak evolution rate, i.e. the end temperature of the peak. Dotted lines indicate R_{LE} of specimens of radius 0.1 mm.

Fig. 6. Variation of R_{LE} parameter with temperature during TDA a) in the center, and b) near the edge of the specimen. Arrows indicate the temperature at which the hydrogen evolution rate fell to one hundredth of the peak evolution rate, i.e. the end temperature of the peak. Dotted lines indicate R_{LE} of specimens of radius 0.1 mm.

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is the dimensionless time, \( c_0 \) is the initial concentration of hydrogen, \( J_0 \) and \( J_1 \) are the Bessel function of the first kind of order zero and the first order, respectively, and \( \alpha_n \)'s are the roots of \( J_0 (\alpha_n r) = 0 \). Kissinger-type desorption is achieved where the 2\( \text{nd} \) and the higher order terms in the r.h.s. of Eq. (8) become negligibly small compared to the first term.\(^5\) The critical time for achieving it is \( \tau = 0.119 \) at which the fraction of hydrogen remaining in the specimen is 0.35 for a cylindrical specimen, see Table 1 of Ref. 6. Under this circumstance it is interesting to see if the Kissinger-type desorption can be achieved in the mixed-control condition.

**Figures 8(a) and 8(b) display the concentration distribution of hydrogen in the lattice and the trap site, respectively, calculated for specimen R2 at various times of pre-exposure at 20°C.** The concentration of trapped hydrogen on the specimen edge is not zero at an early stage because hydrogen atoms can be captured in the trap site from the inside of the specimen. The escape of hydrogen in the trap site is delayed compared to hydrogen in the lattice and this makes \( R_{LE} \) small near the edge at an early stage of pre-exposure. Figure 8(c) shows TDA spectra of the corresponding pre-exposed specimens. It is seen that the peak moves slowly to a higher temperature with exposure time. In experiment the shift of peak in pre-exposed specimens is often attributed to the continuum or multi-energy levels of trap sites in the strain field of dislocation. However, it can happen due to the change of initial hydrogen distribution during exposure even with the trap site of a single energy level. In order to achieve Kissinger-type desorption the time for exposure was taken to be \( t \leq 3 \times 10^5 \) s for specimen R2. Figure 8(d) indicates that with this exposure time \( R_{LE} \) in the center and near the edge becomes close to each other from the beginning, albeit it does not approach unity. As seen in Eq. (9), the pre-exposure time required for achieving Kissinger-type desorption is proportional to the square of specimen diameter. It was thus taken to be \( 5 \times 10^5, 1 \times 10^6 \) and \( 3 \times 10^5 \) s for specimens R1, R3 and R4, respectively. \( E_d \) evaluated from the C-L plot of pre-exposed specimens is shown in Fig. 7 (open circles). It is almost equal to \( E_d^0 \) irrespective of specimen thickness, in other words from detrapping- to diffusion-controlled desorption. Particularly, it is noteworthy that \( E_d = E_d^0 \) even if desorption occurs in a mixed mode or with \( R_{LE} \) significantly below unity.

Choo-Lee plots are often carried out without paying attention to the condition in which desorption occurs. The above results indicate that the slope of the plot or detrap energy differs significantly from the true value (\( E_d^0 \)) due to the influence of initial hydrogen distribution and/or the condition of desorption. It is emphasized that pre-exposure can remove or mitigate very efficiently the influence of these factors. The critical exposure time of a cylindrical specimen is the time at which approximately two thirds of hydrogen escapes from the specimen. Hence, the specimen should not be too thick to avoid an excessively long exposure to achieve Kissinger-type desorption.

**6. Summary**

Thermal desorption analysis (TDA) of hydrogen was carried out in high strength SCM435 steel using cylindrical specimens of radius from 0.5 to 5 mm, aiming to vary the
desorption condition from detrapping- to diffusion-control. The specimens were cathodically charged at ambient temperature until saturated and were heated at a ramp rate from 25 to 200°C/h. All specimens exhibited a single peak except thin specimens in which the evolution rate of hydrogen decreased monotonically at the smallest ramp rate. The trap energy of hydrogen was evaluated from the Choo-Lee (C-L) plot for specimens of each radius. The trap energy obtained from the thinnest specimens ($r_0 = 0.5$ mm) gave a much better account for peak temperatures of all specimens. A significantly lower $E_B$ value for specimens of radius 1.25–5 mm can be attributed to the substantial involvement of lattice diffusion, more specifically the hydrogen distribution prior to TDA. The influence of initial hydrogen distribution can be removed if pre-exposure is carried out for a sufficiently long time even in mixed-control desorption. To evaluate the trap energy of hydrogen thin specimens are preferred because not only the influence of diffusion is reduced, but also the pre-exposure time can be shortened and peak temperatures do not enter the temperature region in which the Arrhenius plot of $D_{ef}$ deviates from the straight line.

Fig. 8. a) Diffusion profiles of hydrogen in the lattice and b) concentration distribution of trapped hydrogen at various exposure times in R2 specimen. c) TDA spectra of pre-exposed specimens for various times at room temperature. d) Comparison of $R_{LE}$ of specimens ($r_0 = 1.25$ mm) with and without pre-exposure. The pre-exposure time was $3 \times 10^4$ s.

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