Diffusion of hydrogen in the TRIP 800 steel

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Abstract

The presented paper is devoted to the study of hydrogen diffusion characteristics in the C-Mn-Si TRIP 800 steel. The steel was tested in three different states: in as-received state after hot and cold rolling and subsequent heat treatment; and furthermore after 5\% and 10\% tensile deformation. Hydrogen diffusion characteristics were studied by means of electrochemical permeation method. Two build up transients corresponding to lower and higher charging current densities as well as a decay transient were recorded during experiment. The lowest values of hydrogen diffusion coefficient (from 1.10^{-7} to 3.5.10^{-7} \text{cm}^{2}\cdot\text{s}^{-1}) were observed during the first build up transient; the value of 3.5.10^{-7} \text{cm}^{2}\cdot\text{s}^{-1} corresponded to 10\% tensile deformation. During the 2\textsuperscript{nd} build up transient corresponding to the higher charging current density, hydrogen diffusion coefficients increased markedly reflecting thus the fact that hydrogen trapping was less pronounced. For decay transients hydrogen diffusion coefficients were situated between values obtained for the 1\textsuperscript{st} and 2\textsuperscript{nd} build up transients. In all studied states, rather high sub-surface hydrogen concentration was observed during the 1\textsuperscript{st} build up transient rising to 12.6 ppm of hydrogen in as-received state. The obtained results are explained taking into account steel microstructure and hydrogen trapping.

Keywords: Hydrogen permeation; TRIP steel; hydrogen embrittlement;

1. Introduction

Recently, new steel grades have been developed, which belong to so-called advanced high strength steels (AHSS). Transformation Induced Plasticity (TRIP) steel represents one kind of AHSS. It demonstrates superior...
mechanical performance of high strength and very good fracture toughness as shown by De Cooman [1]. For these reasons, TRIP steel is regarded as one of the most promising candidates for automotive applications. However, according to Sojka et al. [2] TRIP steel is susceptible to hydrogen embrittlement. The susceptibility to hydrogen embrittlement is closely related to hydrogen diffusion characteristics. Nevertheless, there are only few literature data concerning hydrogen diffusion characteristics in TRIP steels. Ly [3] found out that in the TRIP steel containing approximately 7% of retained austenite the hydrogen diffusion coefficient was rather low (about $1.10^{-7}$ cm$^2$.s$^{-1}$), while the sub-surface hydrogen concentration was higher in comparison with other types of AHSS. Kim et al. [4] performed in-situ observation of changes in the electrochemical hydrogen permeation flux under loading resulting in $\gamma \rightarrow \alpha'$ transformation in C-Mn-Si-Al TRIP steel. According to him hydrogen permeation upon application of a plastic deformation is governed by an initial drop in the permeation current due to hydrogen trapping by newly generated dislocations and subsequently by an increase in the permeation current due to hydrogen transport by dislocations.

In the presented paper hydrogen diffusion characteristics were studied in the C-Mn-Si TRIP 800 steel in three different states: in as-received state after hot and cold rolling and subsequent heat treatment; and furthermore after 5% and 10% tensile deformation.

2. Material and experimental procedure

The C-Mn-Si TRIP 800 steel was used in the form of thin sheets with the thickness of 1.5 mm. The chemical composition of the studied steel is given in Table 1.

### Table 1. Chemical composition of the studied TRIP 800 steel (mass percent).

<table>
<thead>
<tr>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Ni</th>
<th>Cu</th>
<th>Mo</th>
<th>Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>1.48</td>
<td>1.48</td>
<td>0.014</td>
<td>0.004</td>
<td>0.17</td>
<td>0.15</td>
<td>0.06</td>
<td>0.01</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Details concerning steel manufacturing and its heat treatment can be found in [2]. Steel structure was analyzed using light microscopy (LM) and scanning electron microscopy (SEM). Retained austenite content was determined by means of X-ray analysis using Co K$\alpha$ source ($\lambda=0.17902$ nm).

Electrochemical hydrogen permeation tests were carried out using a Devanathan-Stachurski two-component cell separated by a steel membrane - working electrode. The exit side of the working electrode was palladium coated to prevent from hydrogen atom recombination during permeation experiments. Hydrogen charging cell was filled with 0.05M $\text{H}_2\text{SO}_4$, while the exit cell was filled with 0.1 M NaOH solution. The exit cell was de-aerated by argon bubbling before and during experiments. The hydrogen permeation current was recorded using a VOLTALAB 40 potentiostat.

After an output current stabilization, the entry side of the specimen was polarized anodically at a current density of $+35$ mA.cm$^{-2}$. At the end of this period (5 minutes), $\text{H}_2\text{SO}_4$ charging solution was renewed continuously to eliminate metallic ions from the solution. After that, two build-up transients (BUT) were recorded, the first one at the charging current density of $-20$ mA.cm$^{-2}$, the second one at the charging current density of $-35$ mA.cm$^{-2}$. Before ending the experiment hydrogen charging was stopped and a decay transient (DT) was also recorded.

3. Results and discussion

3.1. Microstructure and mechanical properties

From the point of view of LM and SEM the steel microstructure consisted only of ferrite and bainite. The content of retained austenite is shown in Table 2. Details concerning steel microstructure can be found in [2]. Examples of the microstructure are shown for the as-received state and for the state after 10% tensile deformation in Fig. 1 a,b.

Mechanical properties of the TRIP steel are given in Table 2 for all studied states. It can be deduced from Table 2 that tensile deformation resulted in increasing of both yield strength and tensile strength and also in increasing of
$R_p/0.2/R_m$ ratio while the elongation decreased. Retained austenite content dropped from 11.0% in as-received state to 2.2% after 10% tensile deformation.

![Fig.1. Microstructures of the TRIP steel (a) in as received state; (b) after 10% tensile deformation.](image)

### Table 2. Mechanical properties and retained austenite content.

<table>
<thead>
<tr>
<th>State</th>
<th>$R_p/0.2$ [MPa]</th>
<th>$R_m$ [MPa]</th>
<th>$R_p/0.2/R_m$</th>
<th>$A_{25}$ [%]</th>
<th>Retained austenite content [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-received</td>
<td>421</td>
<td>877</td>
<td>0.48</td>
<td>31.2</td>
<td>11.0</td>
</tr>
<tr>
<td>5% deformation</td>
<td>754</td>
<td>919</td>
<td>0.82</td>
<td>25.6</td>
<td>5.5</td>
</tr>
<tr>
<td>10% deformation</td>
<td>963</td>
<td>1009</td>
<td>0.95</td>
<td>17.6</td>
<td>2.2</td>
</tr>
</tbody>
</table>

### 3.2. Hydrogen diffusion characteristics

Hydrogen diffusion coefficients were calculated using the time-lag method according to Eq. 1:

$$D = \frac{L^2}{6 \cdot t_L} \tag{1}$$

where $L$ represents the membrane thickness and $t_L$ corresponds to the time where the permeation current reaches 63% of its steady-state value.

Sub-surface hydrogen concentration was calculated using Eq. 2:

$$C_H^0 = \frac{i_\infty \cdot L}{D \cdot F} \tag{2}$$

where $i_\infty$ is a steady-state current density and $F$ is Faraday’s constant.

For the correlation between experimental results and a theoretical model, Eq. 3 was used to calculate a normalized hydrogen flux $J/J_\infty$:

$$\frac{J_t}{J_\infty} = \frac{2}{\sqrt{\pi} \cdot \tau} \sum_{n=0}^\infty \exp \left[-\frac{(2 \cdot n + 1)^2}{4 \cdot \tau}\right]$$

where $\tau$ is dimensionless time equal to $D \cdot t/L^2$. 
Effective hydrogen diffusion coefficients are shown in Fig. 2 for all three studied states.

Fig. 2. Effective hydrogen diffusion coefficients $D_{\text{eff}}$ for all studied states

It is obvious from Fig. 2 that the lowest values of hydrogen diffusion coefficient were always obtained for the first BUT. It can be related to hydrogen trapping in both reversible and irreversible traps. The hydrogen diffusion coefficient corresponding to the first BUT was higher for the state after 10% tensile deformation. This behavior is in good agreement with results of Kim et al. [4]. According to him formation of martensite facilitates hydrogen diffusion in the TRIP steel. Hydrogen diffusion coefficients corresponding to the second BUT were markedly higher and confirmed that probably most of traps were filled by hydrogen during the first BUT. Nevertheless, values of hydrogen diffusion coefficients still remained lower in comparison with conventional steels having bcc lattice. For decay transients hydrogen diffusion coefficients were usually situated between values obtained for the 1st and 2nd BUT. The obtained results are in a good agreement with findings of Zakroczymski [5]. According to him during the first BUT hydrogen trapping can be expected and during DT hydrogen detrapping can be expected, influencing thus values of hydrogen diffusion coefficient. Examples of fitting experimental results with the theoretical curves of normalized hydrogen flux $J_t/J_\infty$ are shown in Figs. 3-5 for the as-received state. Measured data fitted very well with the theoretical curves for the second BUT in all studied states (Fig. 3). However, for the first BUT (Fig. 4) and for the DT (Fig. 5), the measured data were shifted to longer times in comparison with the theoretical curves confirming thus the important role of hydrogen trapping and detrapping [5].

Fig. 3. Fitting the experimental data with the theoretical curve for the 2nd BUT in as-received state.
Hydrogen sub-surface concentration was calculated for the first BUT using Eq. 2. The obtained results are presented in Table 3. The hydrogen sub-surface concentration was rather high mainly if the amount of retained austenite in the structure was not too low. In this way the role of retained hydrogen as an important and very probably irreversible hydrogen trap is confirmed. The high sub-surface concentration of hydrogen in the studied TRIP steel can, at least partially, explain its rather high susceptibility to hydrogen embrittlement found by Sojka et al. [2].

Table 3. Hydrogen sub-surface concentration during the 1st build up transient (mass ppm).

<table>
<thead>
<tr>
<th></th>
<th>As-received</th>
<th>5 % tensile deformation</th>
<th>10 % tensile deformation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen ppm</td>
<td>12.6</td>
<td>12.1</td>
<td>5.4</td>
</tr>
</tbody>
</table>

Fig. 4. Fitting the experimental data with the theoretical curve for the 1st BUT in as-received state.

Fig. 5. Fitting the experimental data with the theoretical curve for the DT in as-received state.
4. Conclusions

The presented results of the study of hydrogen diffusion characteristics in the C-Mn-Si TRIP 800 steel in three different states can be summarized as follows:

The values of hydrogen diffusion coefficients in the TRIP 800 steel were rather low and lay between $1.10^{-7}$ cm$^2$.s$^{-1}$ and $7.8.10^{-7}$ cm$^2$.s$^{-1}$.

The highest values of hydrogen diffusion coefficient were observed during the 2nd build up transient where the role of hydrogen trapping was limited.

The decrease of retained austenite content resulted in the increase of hydrogen diffusion coefficient.

The comparison of experimental data with the theoretical model showed a good fitting for the 2nd build up transient, while during the 1st build up transient and during the decay transient a shift of experimental data to longer time was observed due to hydrogen trapping and detrapping.

Rather high sub-surface concentration of hydrogen was determined in the studied steel especially for states with higher retained austenite content.

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References