DIFFUSION CHARACTERISTICS OF HYDROGEN IN THE TRIP 800 C-Mn-Si-P STEEL

Jaroslav SOJKA, Petr ŠTĚPÁN, Petra VÁŇOVÁ

VŠB – Technical University of Ostrava, Faculty of Metallurgy and Materials Engineering, 17. listopadu 15, CZ 708 33 Ostrava, Czech Republic, jaroslav.sojka@vsb.cz, petr.stepan@vsb.cz, petra.vanova@vsb.cz

Abstract

The presented contribution is devoted to evaluation of hydrogen diffusion characteristics in the TRIP 800 steel, based on C-Mn-Si-P composition, i.e. in steel with increased phosphorus content. Steel was studied after standard heat treatment, including intercritical annealing and annealing in the range of bainitic transformation. Hydrogen diffusion characteristics in the TRIP 800 steel were obtained by means of electrochemical permeation method. Specimens were used in the form of thin discs with thickness of 0.5 mm approximately. The output sides of specimens were palladium coated to prevent hydrogen recombination when leaving specimen. Diffusion characteristics of hydrogen were obtained by recording output current density as a function of time. Experimental procedure included preliminary hydrogen charging followed by polarization reversion to activate specimen surface. After that two hydrogen chargings were performed with an increasing current density. Hydrogen diffusion coefficient in the TRIP 800 steel was calculated from all build-up transients and also from a decay transient at the end of experiment. The lowest hydrogen diffusion coefficient was observed at the first hydrogen charging, which reflected hydrogen trapping during this period of experiment. The highest measured hydrogen diffusion coefficient was recorded during last hydrogen charging. Its value was $5 \times 10^{-7}$ cm$^2$·s$^{-1}$ approximately, which is much lower in comparison with common steels having bcc crystal lattice. This fact can be attributed to the presence of about 9 % of retained austenite in the structure of the steel. Subsequently, hydrogen surface concentration at the input surface was calculated, giving very high level in tens ppm of H.

Keywords: Hydrogen embrittlement, TRIP steel, electrochemical permeation of hydrogen.

1. INTRODUCTION

Transformation induced plasticity (TRIP) steel represents a type of advanced high-strength steel which demonstrates superior mechanical performance of high strength and very good fracture toughness. The properties of TRIP steels depend on an optimal chemical composition, and it is essential to include elements that inhibit cementite and/or carbide precipitation to ensure that a sufficient quantity of retained austenite (RA) remains in the steel microstructure at ambient temperature [2]. The optimal content of retained austenite is in the range 10%-15% [1,2]. Conventional TRIP steel alloying elements are: Mn (approx. 1.5 wt%), Si (approx. 1.5 wt%), and/or Al, which can more or less substitute for Si [3, 4]. TRIP steels containing phosphorus have also been tested in other works [5]. The use of different elements is related to their influence on hot-dip galvanizing. The carbon content of TRIP steels with a tensile strength up to 1000 MPa is approx. 0.2 wt% [1]. Optimal mechanical properties are achieved using a proper heat treatment that usually includes a two-step annealing: intercritical annealing and annealing in the region of the bainitic transformation. During both annealing processes, the retained austenite is enriched by carbon up to 1.0% or even more [1]. This provides stability to the austenite at ambient temperatures [2]. However, TRIP steels are susceptible to hydrogen embrittlement and also to delayed fracture. Only few works were devoted to the hydrogen embrittlement of the TRIP steels [6-8]. Hydrogen embrittlement is influenced by diffusion characteristic of hydrogen in steels. In this field, however, information is really sporadic [9,10]. Ly studied [9] hydrogen diffusivity in C-Mn-Si TRIP 800 steel by means of electrochemical permeation of hydrogen. She
found rather low hydrogen diffusion coefficient in the studied steel; on the contrary surface concentration of hydrogen was very high compared to different advanced high strength steels (AHSS). Kim et al. [10] performed in-situ observation of the change in hydrogen permeation in C-Mn-Si-Al TRIP steel. The lowest value of hydrogen diffusion coefficient was observed in the state with 13.2 % of retained austenite (RA), while the highest value was determined after straining resulting in 0 % of RA.

The aim of the presented paper is to evaluate hydrogen diffusion characteristics in the C-Mn-Si-P TRIP 800 steel by means of the electrochemical permeation method. A special procedure of hydrogen permeation was used to be able to analyze correctly the surface concentration of hydrogen, too.

2. EXPERIMENTAL

Experiment was performed on the TRIP 800 steel based on C-Mn-Si composition but with increased phosphorus content. Chemical composition of the investigated steel is given in Table 1.

<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>V</th>
<th>Al</th>
<th>Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>1.50</td>
<td>1.50</td>
<td>0.050</td>
<td>0.005</td>
<td>0.16</td>
<td>0.15</td>
<td>0.06</td>
<td>0.02</td>
<td>0.006</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Initial material was prepared as laboratory heat with the ingot mass of 150 kg. Details concerning further manufacturing of the material were given in [11]. The final product represented sheets with thickness of 1.50 mm. Investigated steel displayed following mechanical properties in the initial state: yield strength $R_p0.2 = 417$ MPa; ultimate tensile strength $R_m = 944$ MPa and elongation at fracture $A_{50} = 24 %$.

Microstructure of the studied steel was observed by means of 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).

The electrochemical hydrogen permeation tests were carried out using a Devanathan-Stachurski two-component cell separated by the steel membrane – working electrode. Both sides of the working electrode were polished mechanically up to 1200 grinding paper. After that, exit side of the working electrode was palladium coated to prevent from the hydrogen atom recombination during permeation experiments [12]. Hydrogen charging cell was filled with 0.05M H$_2$SO$_4$. The hydrogen exit cell was filled with 0.1 M NaOH solution. Both cells were de-aerated by argon bubbling before and during experiments. At the beginning of the experiment open circuit potential (OCP) was measured at the exit cell using a saturated sulfate electrode (SSE) as a reference electrode and a platinum wire as an auxiliary electrode. After measuring OCP exit surface of the working electrode was polarized anodically to a value higher to 50 mV with respect to OCP. The hydrogen permeation current was recorded using a VOLTALAB 10 potentiostat during experiments.

After residual current stabilization, first, preliminary permeation transient was performed at a charging current density of -15 mA·cm$^{-2}$. After the permeation current reached its steady-state level, the entry side was polarized anodically at a current density of + 35 mA·cm$^{-2}$ to refresh the membrane surface by an anodic dissolution and to extract, at least partially, diffusive hydrogen. At the end of this period (5 – 10 minutes), H$_2$SO$_4$ charging solution was renewed continuously to eliminate metallic ions. After that, two build-up transients were recorded, the first one at the charging current density of -15 mA·cm$^{-2}$, the second one at the charging current density of -30 mA·cm$^{-2}$. Before ending the experiment the charging was stopped and a decay transient was also recorded. The apparatus used for hydrogen electrochemical permeation measurements is shown in Fig. 1.
Fig. 1 The apparatus used for electrochemical permeation of hydrogen

3. RESULTS AND DISCUSSION

3.1 Microstructure

Microstructure of the studied steel was the same from the viewpoint of both light and scanning electron microscopy. The fine-grain microstructure consisted predominantly of proeutectoid ferrite and bainite. In some locations, it was possible to assume the presence of small regions of martensite. It was impossible to identify any retained austenite using either light or scanning electron microscopy. The average grain size of ferrite was determined as the mean intercept length using digital image analysis employing the Image ProPlus software package. The mean intercept length of ferritic grains was 4.5±0.5 μm. The percentage area of ferrite was evaluated by point counting method and its value was 51±2%. An example of the microstructure obtained using light microscopy after Nital etching is shown in Fig. 2a and only regions of ferrite and bainite can be clearly distinguished in this micrograph. In Fig. 2b, microstructure observed by SEM is presented. To a small extent, non-metallic inclusions were observed in the studied steel. These inclusions were identified as either aluminum oxides, or manganese sulfides.

The content of retained austenite was determined using X-ray diffraction analysis. A mean value of 9.0±2.0 % of RA was obtained for the studied steel.

3.2 Electrochemical permeation of hydrogen

An example of hydrogen permeation curve is shown in Fig. 3. It shows that during the first permeation the output current density, i.e. the hydrogen flux, is the lowest. Much higher values of hydrogen flux are observed for the two build-up transients that follow the period of anodic dissolution. It can be deduced from the curve that the entry of hydrogen is really inhibited during the first permeation, which was already described by Jerome [12]. This behavior is attributed to the passivation of the surface in an acid environment. The hydrogen entry is accelerated after the anodic dissolution of the entry side is performed.
After the second build-up transient the steady-state current decreases considerably in time. This can be related to changes of the entry side of the specimen (working electrode) [12].

**Fig. 2a** Microstructure of the TRIP steel (LM)  
**Fig. 2b** Microstructure of the TRIP steel (SEM)

**Fig. 3** Example of hydrogen permeation curve for the C-Mn-Si-P TRIP steel

Hydrogen diffusion coefficients $D$ were calculated using the time-lag method according to the following equation:

$$D = \frac{L^2}{6t_L};$$

(1)

where $L$ is a membrane thickness and $t_L$ corresponds to the point where the permeation current reaches 63 % of its steady-state value. Surface hydrogen concentration $C_{H^0}$ was calculated by the following equation:
\[ C_H^0 = \frac{i_w L}{DF}; \]  \hspace{1cm} (2)

where \( i_w \) is a steady-state current and \( F \) is Faraday’s constant.

Obtained results of hydrogen diffusion coefficients \( D \) and surface hydrogen concentration \( C_H^0 \) are summarized in Table 2.

**Tab. 2 Results of hydrogen diffusion coefficients \( D \) and surface hydrogen concentration \( C_H^0 \)**

<table>
<thead>
<tr>
<th>Order of permeation</th>
<th>Diffusion coefficient of hydrogen ((\text{cm}^2 \cdot \text{s}^{-1}))</th>
<th>Surface concentration of hydrogen ((\text{mol} \text{ H} \cdot \text{m}^{-3}))</th>
<th>Surface concentration of hydrogen ((\text{mass ppm}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preliminary permeation</td>
<td>9.5 \times 10^{-8}</td>
<td>was not calculated</td>
<td>was not calculated</td>
</tr>
<tr>
<td>1(^{st}) build-up transient (-15 mA cm(^{-2}))</td>
<td>2.0 \times 10^{-7}</td>
<td>160</td>
<td>20.3</td>
</tr>
<tr>
<td>2(^{nd}) build-up transient (-30 mA cm(^{-2}))</td>
<td>5.6 \times 10^{-7}</td>
<td>184</td>
<td>24.4</td>
</tr>
<tr>
<td>Decay transient</td>
<td>3.3 \times 10^{-7}</td>
<td>65</td>
<td>8.3</td>
</tr>
</tbody>
</table>

It is evident from Table 2 that hydrogen diffusion coefficient corresponding to the preliminary permeation is extremely low for a steel having in majority bcc crystal lattice. This low value of \( D \) can be attributed to the fact that hydrogen, during his passage through the membrane, must fill all kinds of traps, both reversible and irreversible. Interface between retained austenite and the matrix represents the most important irreversible traps in the TRIP steels. The values obtained for the 1\(^{st}\) and 2\(^{nd}\) build-up transients as well as for decay transient are higher by one order in comparison with preliminary permeation. These values are in good agreement with values that Ly [9] found for C-Mn-Si TRIP steel \((1.3 – 6.9 \times 10^{-7} \text{ cm}^2 \cdot \text{s}^{-1})\) and also with the value that Kim and al. [10] observed for C-Mn-Si-Al TRIP steel containing 13.2% of RA. In [10] the value of hydrogen diffusion coefficient was 1.0 \times 10^{-7} \text{ cm}^2 \cdot \text{s}^{-1}, which is value very close to that we found for the first, preliminary build-up transient. Our study also confirmed very high values of surface hydrogen content found by Ly [9]. Ly found surface hydrogen concentration in order of tens wt. ppm for the C-Mn-Si TRIP 800 steel, which was much higher than surface hydrogen concentration for other AHSS she studied. We can deduce from these results that a higher concentration of diffusible hydrogen can be expected in the TRIP steels. As equilibrium exists between the concentration of diffusible hydrogen and reversibly trapped hydrogen, the higher the concentration of diffusible hydrogen, the higher will also be the concentration of reversibly trapped hydrogen. Accepting this concept, we can expect high hydrogen concentration around all sites in the TRIP steels, which can provoke hydrogen embrittlement, e.g. around non-metallic inclusions. In this way it is possible to explain rather high level of hydrogen embrittlement of the TRIP steels found in [6] for high hydrogen contents.

### 4. CONCLUSIONS

The presented paper was devoted to evaluation of diffusion characteristic of hydrogen in C-Mn-Si-P TRIP 800 steel tested by electrochemical permeation method. A special procedure was performed to overcome some difficulties of this technique. The obtained results can be summarized as follows:

- During the first, preliminary permeation a weak value of hydrogen diffusion coefficient was observed, very probably due to the fact that all kinds of traps had to been filled during the passage of hydrogen through the membrane. Furthermore, the hydrogen flux was very low too, which can be attributed to the passivation of the membrane entry side, which hindered hydrogen entry.
The other build-up transients, as well as decay transient gave values of hydrogen diffusion coefficient between $2.0 \times 10^{-7}$ cm$^2$·s$^{-1}$ and $5.6 \times 10^{-7}$ cm$^2$·s$^{-1}$ which are in good agreement with results for other TRIP steels (C-Mn-Si and C-Mn-Si-Al).

High surface hydrogen concentration was observed for the studied steel which is also in agreement with results for other studied TRIP steels and which can explain rather high susceptibility of TRIP steels to hydrogen embrittlement despite the higher retained austenite content.

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