

HYDROGEN DIFFUSION IN THE TRIP 800 STEEL WITH HIGHER PHOSPHORUS CONTENT – EFFECT OF DEFORMATION

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Abstract

Hydrogen diffusion characteristics were studied in C-Mn-Si TRIP 800 steel containing 0.05 mass % of phosphorus. The steel was tested in as-received state and also in states corresponding to 5 and 10 % tensile deformation. Steel microstructure was analyzed by light microscopy, scanning electron microscopy and X-ray diffraction. 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 permeation experiments. In the as-received state, steel microstructure consisted of ferrite, bainite and approx. 14 % of retained austenite. The tensile deformation resulted in a decrease of retained austenite content and in a considerable increase of yield and tensile strength. Hydrogen diffusion coefficients of the studied TRIP steel varied from $1.6 \times 10^{-7} \text{ cm}^2 \cdot \text{s}^{-1}$ to $1.3 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$. The lowest values corresponded to the as-received state – without deformation; the highest ones corresponded to 5 % tensile deformation. For one state, the lowest values of hydrogen diffusion coefficient were observed during the first build up transient. During the second 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 1st and 2nd build up transients. Very high sub-surface hydrogen concentrations (up to 35 ppm) were obtained from the permeation results.

Keywords: TRIP steel, hydrogen diffusion, electrochemical permeation method

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 [1]. For these reasons, TRIP steel is regarded as one of the most promising candidates for automotive applications. TRIP steels are based on the C-Mn-Si chemical composition in most cases. Nevertheless, silicon may cause serious difficulties during hot-dip galvanizing. For this reason, silicon can be partially or totally replaced by aluminum [2]. Variants of TRIP steels have also been developed with high phosphorus content, again to improve conditions of hot-dip galvanizing and to facilitate retained austenite stabilization [3]. The appropriate amount of retained austenite in the TRIP steels (10-15%) is essential with respect to optimal mechanical properties [1]. All kinds of TRIP steels seem to be susceptible to hydrogen embrittlement [4-6]. This problem has got practical importance as there is a risk of hydrogen embrittlement during acid pickling, an operation preceding hot-dip galvanizing. Recently, Zhu et al. [7] found out that the resistance of the TRIP steels to hydrogen embrittlement can be improved by cryogenic and tempered treatment. The authors attributed this

improvement to a higher stability of remained retained austenite during straining as hydrogen induced cracks always initiated from the fresh untempered martensite formed during plastic deformation. Depover et al. [8] studied susceptibility to hydrogen embrittlement in several kinds of advanced high strength steels using slow strain rate tests. They found out that TRIP steel was the most susceptible to hydrogen embrittlement of all studied materials. The authors correlated that behavior to the fact that retained austenite represents a deep, irreversible trap for hydrogen in the TRIP steel and martensite formed during deformation, which inherits this high amount of hydrogen, becomes extremely brittle. Hyun Ryu et al. [9] studied hydrogen trapping in the TRIP steels with different retained austenite stability. They showed that retained austenite serves as a deep trapping site in the TRIP steels. After $\gamma \rightarrow \alpha'$ transformation hydrogen becomes more mobile and can provoke hydrogen embrittlement of the TRIP steel. The susceptibility to hydrogen embrittlement in the TRIP steels is thus closely related to hydrogen diffusion characteristics. Nevertheless, there are still only few literature data concerning hydrogen diffusion in the TRIP steels. Ly [10] found out that in the C-Mn-Si TRIP steel containing approximately 7% of retained austenite the hydrogen diffusion coefficient was rather low (about $1 \times 10^{-7} \text{ cm}^2 \cdot \text{s}^{-1}$), while the sub-surface hydrogen concentration was higher in comparison with other types of AHSS. Kim et al. [11] performed in-situ observation of the change 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 a plastic deformation is governed by an initial drop in the permeation flux due to hydrogen trapping by newly generated dislocations and subsequently by an increase in the permeation flux due to hydrogen transport by dislocations.

In the presented paper hydrogen diffusion characteristics were studied in the C-Mn-Si TRIP 800 steel with increased phosphorus content (0.05 mass %) in three different states: in the as-received state after hot and cold rolling and subsequent heat treatment; and furthermore after 5% and 10% tensile deformation to be able to take different retained austenite contents into account.

2. MATERIAL AND EXPERIMENTAL PROCEDURE

The C-Mn-Si-P 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 %)

C	Mn	Si	P	S	Cr	Ni	Cu	V	Al	Nb
0.20	1.50	1.50	0.050	0.005	0.16	0.15	0.06	0.02	0.006	0.02

Details concerning steel manufacturing and its heat treatment can be found in [4]. Steel structure was observed using light microscopy (LM) and scanning electron microscopy (SEM). Retained austenite (RA) content was determined by means of X-ray analysis using Co K_{α} source ($\lambda=0.17902 \text{ nm}$). Mechanical properties were determined using a standard tensile test.

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. The hydrogen charging cell was filled with 0.05M H_2SO_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 during experiments.

After an output current stabilization, the entry side of the specimen was polarized anodically at a current density of $+35 \text{ mA} \cdot \text{cm}^{-2}$. At the end of this period (5 minutes), H_2SO_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 $-20 \text{ mA} \cdot \text{cm}^{-2}$, the second one at the charging current

density of $-35 \text{ mA} \cdot \text{cm}^{-2}$. Before ending the experiment hydrogen charging was stopped and a decay transient (DT) was also recorded. This procedure was modified with respect to the previous results [12] to shorten the time of experiments and to overcome some disadvantages of the procedure used before.

3. RESULTS AND DISCUSSION

3.1. Microstructure and mechanical properties

From the point of view of LM and SEM the steel microstructure consisted of ferrite and bainite only. In some micrographs, presence of martensite was also revealed using SEM. Examples of the microstructure of the studied TRIP steel are shown in Figs. 1a, b for the as-received state and for the state after 10% tensile deformation. The content of retained austenite is shown in Table 2 together with the mechanical properties. The retained austenite content dropped from 14.9 % in the as-received state to 7.1 % after 10% tensile deformation. The values of the retained austenite content after deformation are higher in comparison with the C-Mn-Si TRIP steel studied previously [13], which confirms the role of phosphorus as a retained austenite stabilizer [1,3].

The mechanical properties of the studied 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 $R_{p0.2} / R_m$ ratio while the elongation at fracture decreased. Nevertheless, even after 10% tensile deformation the elongation can still be considered as rather high with respect to the values of the yield and tensile strength.

Table 2 Mechanical properties and retained austenite content

State	$R_{p0.2}$ [MPa]	R_m [MPa]	$R_{p0.2}/R_m$	A_{25} [%]	Retained austenite content [%]
as-received	401	925	0.43	27.2	14.9 ± 2.0
5% deformation	764	968	0.79	22.4	11.3 ± 2.0
10% deformation	965	1066	0.91	17.4	7.1 ± 2.0

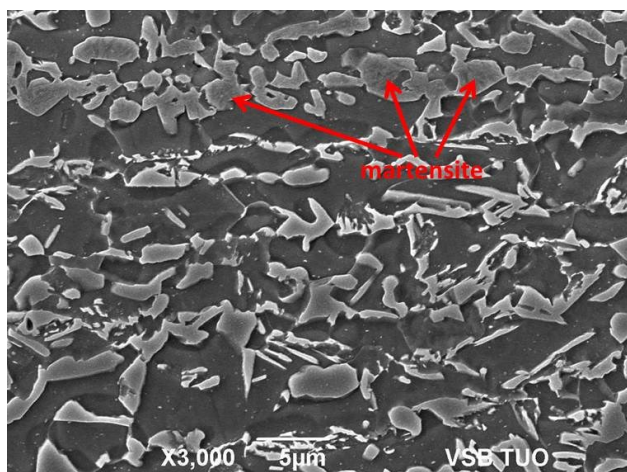


Fig. 1a Microstructure of as-received state (SEM)

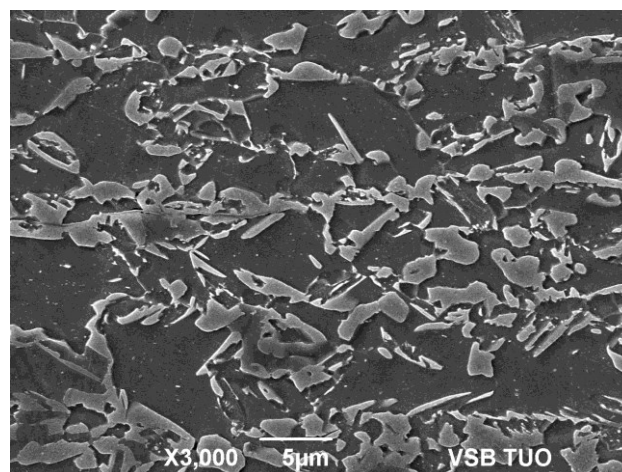


Fig. 1b Microstructure after 10% deformation (SEM)

3.2. Hydrogen diffusion characteristics

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

$$D_{eff} = \frac{L^2}{6t_L}, \quad (1)$$

where L represents the specimen 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:

$$C_H^0 = \frac{i_\infty L}{D_{eff} F}, \quad (2)$$

where i_∞ is the steady-state current density and F is Faraday's constant.

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

$$\frac{J_t}{J_\infty} = \frac{2}{\sqrt{\pi\tau}} \sum_{n=0}^{\infty} \exp \left[-\frac{(2n+1)^2}{4\tau} \right], \quad (3)$$

where τ is the dimensionless parameter equal to $D_{eff} \cdot t / L^2$.

The hydrogen diffusion coefficients are shown in Fig. 2 for all three studied states.

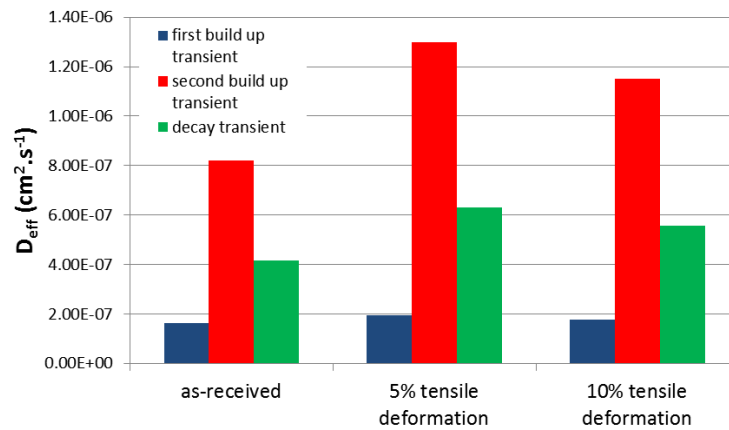


Fig. 2 Effective hydrogen diffusion coefficients D_{eff} for all studied states

It can be deduced from Fig. 2 that the lowest values of hydrogen diffusion coefficient were obtained for the first BUT in all studied states. This fact can be related to the extensive hydrogen trapping in both reversible and irreversible traps during the 1st BUT. The hydrogen diffusion coefficients corresponding to the 1st BUT were only a little bit higher for the state after tensile deformation. Hydrogen diffusion coefficients corresponding to the 2nd BUT were markedly higher in all states in comparison with the 1st BUT and confirmed thus that the major part of traps was filled by hydrogen during the 1st BUT. In the case of the 2nd BUT hydrogen diffusion coefficients were higher for the states after tensile deformation. This behavior is in a good agreement with the results of Kim et al. [11]. According to him formation of martensite facilitates hydrogen diffusion in the TRIP steel. The question arises why the highest value of hydrogen diffusion coefficient corresponds to the 5 % deformation and not to 10 % deformation. Further experiments will be needed in this field but probably hydrogen diffusion may be decelerated by increased dislocation density in the state corresponding to 10 % tensile deformation. Nevertheless, even in the 2nd BUT the values of hydrogen diffusion coefficient still remained lower in comparison with conventional steels having bcc lattice. For the decay transients the hydrogen diffusion coefficients were situated between the values obtained for the 1st and 2nd BUT. The obtained results are in a good agreement with the findings of Zakroczymski [14]. According to him during the 1st BUT extensive hydrogen trapping can be expected and during DT hydrogen detrapping from reversible traps can be expected, influencing thus values of hydrogen diffusion coefficient.

An example of fitting the experimental results with the theoretical curve of normalized hydrogen flux J_t / J_∞ calculated according to Eq. 3 is shown in Fig. 3 for the 2nd BUT in the as-received state. Measured data fitted quite well with the theoretical curves for the 2nd BUT in all studied states. However, for the 1st BUT and for the DT, the measured data were usually shifted to longer time in comparison with the theoretical curves confirming thus the important role of hydrogen trapping and detrapping during the 1st BUT and during DT [14].

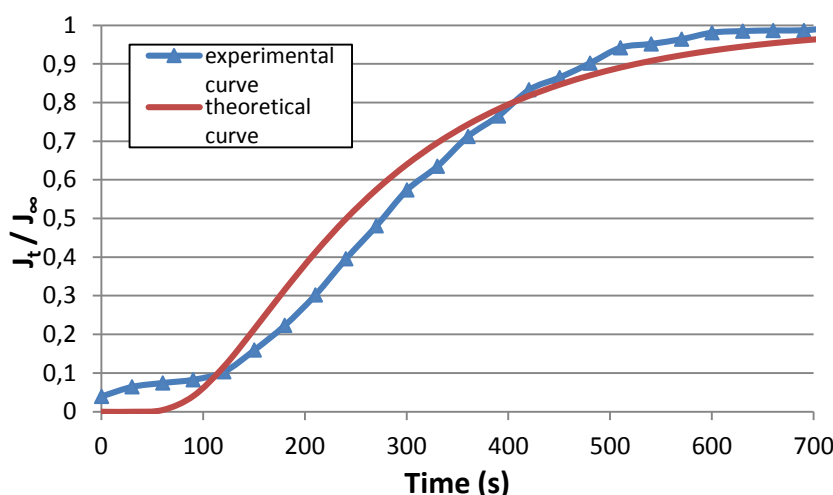


Fig. 3 Fitting the experimental data with the theoretical curve for the 2nd BUT after 5% deformation

Hydrogen sub-surface concentrations were calculated for the 1st BUT using Eq. 2. The obtained results are presented in Table 3. The hydrogen sub-surface concentrations were very high for all studied states. Taking into account that a non-negligible amount of retained hydrogen was present in all states the role of retained hydrogen as an important and irreversible hydrogen trap was confirmed. Undoubtedly, the sub-surface concentration will also be influenced by the surface state, which may vary during experiment. The high sub-surface concentration of hydrogen in the studied TRIP steel can, at least partially, explain rather high susceptibility of the TRIP steels to hydrogen embrittlement [4-9].

Table 3 Hydrogen sub-surface concentration during the first build up transient (mass ppm of H)

As-received	5 % tensile deformation	10 % tensile deformation
20.9	36.9	27.0

4. CONCLUSIONS

The results obtained in the presented work can be summarized in the following way:

The tensile deformation of the TRIP steel with increased phosphorus content manifested itself by a significant increase of the yield strength and ultimate tensile strength while the elongation at fracture decreased only slightly, from 27.2 % in the as-received state to 17.4 % after 10 % tensile deformation. Simultaneously, the content of retained austenite dropped from 14.9 % to 7.1 %.

The effective hydrogen diffusion coefficient was rather low in the as-received state and corresponded to the value $8.1 \times 10^{-7} \text{ cm}^2 \cdot \text{s}^{-1}$ (the value for the 2nd BUT). After the tensile deformation the effective hydrogen diffusion coefficient became higher and corresponded to the values $1.30 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$ for 5% tensile deformation and $1.15 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$ for 10 % tensile deformation. This result confirms that the formation of martensite in the TRIP steels results in an increase of hydrogen mobility. The fact that after 10 % tensile

deformation the hydrogen diffusion coefficient was a little bit lower than after 5 % tensile deformation can be related to the higher dislocation density after 10 % deformation reducing thus hydrogen mobility.

A very high sub-surface concentration of hydrogen was determined in the C-Mn-Si-P TRIP steel for all studied states. This phenomenon is related to the presence of retained austenite in the steel and can, at least partially, explain rather high susceptibility of the TRIP steels to hydrogen embrittlement.

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