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THE EFFECT OF DEFORMATION ON THE CHANGE OF HYDROGEN DIFFUSION IN C-Mn-Si-P TRIP 800 STEEL

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Hydrogen diffusion characteristics were studied in C - Mn - Si - P TRIP 800 steel. The steel was tested in as-received state and in states after 5 and 10 % tensile deformation. The steel microstructure consisted predominantly of ferrite, bainite and retained austenite. The tensile deformation resulted in a decrease of the retained austenite content. Hydrogen diffusion characteristics were studied by means of electrochemical permeation method for two current densities in build-up transients. Hydrogen diffusion coefficients of the studied TRIP steel varied from $1,6 \cdot 10^{-7}$ cm$^2 \cdot$s^{-1} for the as-received state to $1,3 \cdot 10^{-6}$ cm$^2 \cdot$s^{-1} for the state after 5 % tensile deformation. The hydrogen diffusion coefficients increased markedly during the second build-up transient reflecting thus the fact that hydrogen trapping was less pronounced.

Key words: TRIP steel, deformation, hydrogen, diffusion, electrochemical permeation method

INTRODUCTION

Recently, new steel grades were developed, which belong to the so-called advanced high strength steels (AHSS). TRansformation-Induced Plasticity (TRIP) steel represents one kind of AHSS. It demonstrates superior mechanical performance of the high strength and very good fracture toughness [1,2]. For these reasons, TRIP steel is regarded as one of the most promising candidates for automotive applications. TRIP steels are based on theC - 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 [3]. Variants of TRIP steels have also been developed with higher phosphorus content, again to improve conditions of hot-dip galvanizing and to facilitate stabilization of retained austenite [4]. Appropriate amount of the retained austenite in the TRIP steels (10 - 15 %) is essential for achievement of optimal mechanical properties [1,2]. All kinds of TRIP steels seem to be susceptible to hydrogen embrittlement [5-7]. This problem has practical importance as there is a risk of hydrogen embrittlement during acid pickling, an operation preceding hot-dip galvanizing. Depover at al. [8] studied susceptibility to the 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 the 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 it can provoke hydrogen embrittlement of the TRIP steel. The susceptibility to hydrogen embrittlement in the TRIP steels is thus closely related to characteristics of hydrogen diffusion [10].

In the presented paper the characteristics of hydrogen diffusion 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 in order to be able to take into account different retained austenite contents.

EXPERIMENTAL METHOD

The C - Mn - Si - P TRIP 800 steel was used in the form of thin sheets with the thickness of 1,5 mm. Chemical composition of the studied steel is given in Table 1.

Details concerning steel manufacturing and its heat treatment can be found in [5]. 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_a source (l = 0,17902 nm). Mechanical properties were determined using a standard tensile test.

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Table 1 **Chemical composition of the studied TRIP 800 steel / wt. %**

TRIP 800	C	Mn	Si	P	S
	0,20	1,50	1,50	0,050	0,005
Cr	Ni	Cu	V	Al	Nb
0,16	0,15	0,06	0,02	0,006	0,02

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 atom recombination during permeation experiments from hydrogen. The hydrogen charging cell was filled with 0,05 M 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 stabilization of the output current, the entry side of specimen was polarized anodically at the current density of + 35 mA·cm^{-2}. At the end of this period (5 minutes), H_2SO_4 charging solution was renewed continuously in order 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 end of the experiment the hydrogen charging was stopped and a decay transient (DT) was also recorded.

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 Figure 1 for the as-received state and in Figure 2 for the state after 10 % tensile deformation. The content of retained austenite is shown in Table 2 together with 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 [11], which confirms the role of phosphorus as a retained austenite stabilizer [1,4].

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 an increase of both yield strength and tensile strength and also in an increase 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} / %	RA 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	1 066	0,91	17,4	7,1 ± 2,0

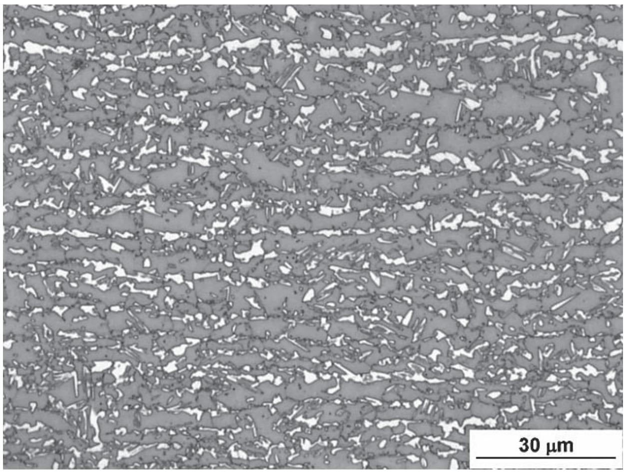

Figure 1 Microstructure of the as-received state (LM, etch. LePera)

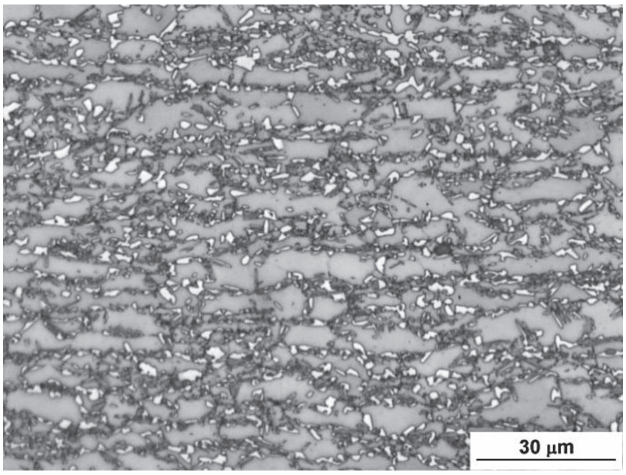

Figure 2 Microstructure after 10 % tensile deformation (LM, etch. LePera)

RESULTS AND DISCUSSION

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

$$D_{\mathrm{eff}} = \frac{L^2}{6t_{\mathrm{L}}}, \tag{1}$$

where L represents the specimen thickness and t_{L} corresponds to the time when the permeation current reaches 63 % of its steady-state value. An example of the permeation curve for the TRIP 800 steel after 5 % deformation is shown in Figure 3.

Sub-surface hydrogen concentration was calculated using Equation 2:

$$C_{\mathrm{H}}^{0} = \frac{i_{\infty} \cdot L}{D_{\mathrm{eff}} \cdot F}, \tag{2}$$

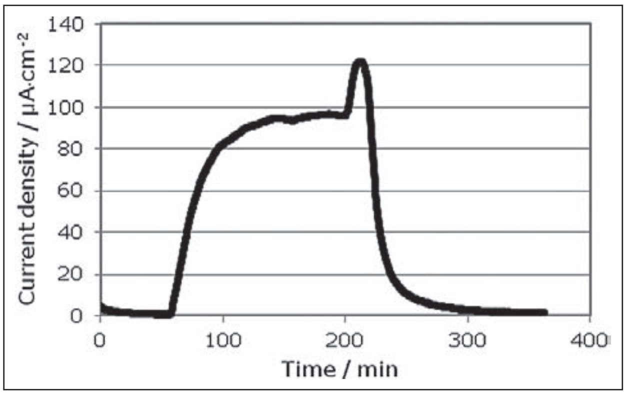

Figure 3 Permeation curve for the TRIP 800 steel after 5 % tensile deformation

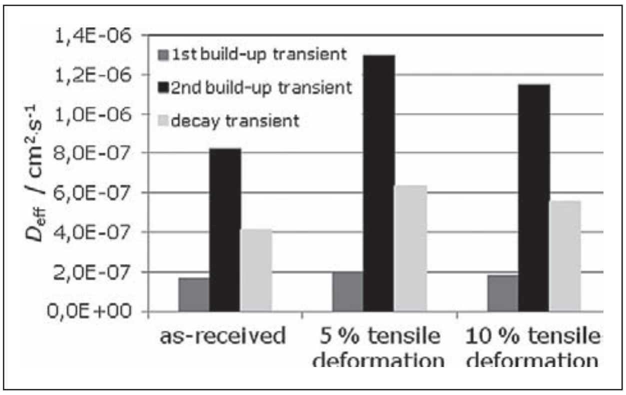

Figure 4 Effective hydrogen diffusion coefficients D_{eff} for all studied states

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

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

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

where t is a dimensionless parameter equal to $(D_{\text{eff}} \times t)/L^2$.

The hydrogen diffusion coefficients are shown in Figure 4 for all three studied states.

It can be deduced from Figure 4 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. [10]. 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 respect but hydrogen diffusion may be probably decelerated by the 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 good agreement with the findings of Zakroczymski [12]. 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 Equation 3 is shown in Figure 5 for the 2nd BUT in the as-received state. The measured data fitted quite well with the theoretical curves for the 2nd BUT in all the 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 [12].

Hydrogen sub-surface concentrations were calculated for the 1st BUT using Equation 2. The obtained results are presented in Table 3. The hydrogen sub-surface concentrations were very high for all the studied states. Taking into account that a non-negligible amount of retained austenite was present in all states the role of retained austenite 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 [5-8].

Table 3 **Hydrogen sub-surface concentration during the first build-up transient / wt. ppm of H**

As-received	5 % tensile deformation	10 % tensile deformation
20,9	36,9	27,0

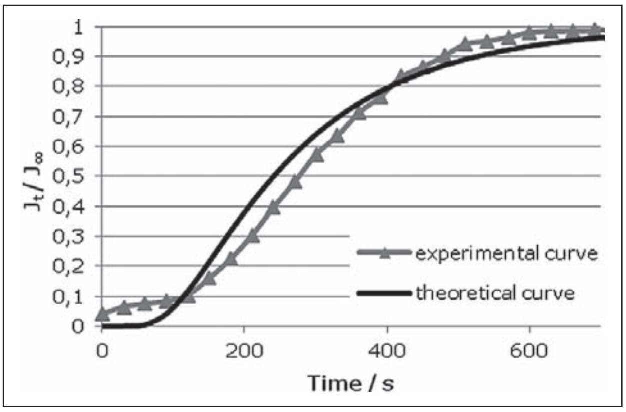

Figure 5 Fitting the experimental data with the theoretical curve for the 2nd BUT after 5 % tensile deformation

CONCLUSIONS

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

Tensile deformation of the TRIP steel with increased phosphorus content manifested itself by the significant increase of the yield strength and ultimate tensile strength while elongation at fracture decreased only slightly, from 27,2 % in the as-received state to 17,4 % after 10 % tensile deformation. At the same time 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 it corresponded to the value of $8{,}1 \cdot 10^{-7}$ $cm^2 \cdot s^{-1}$ (the value for the 2nd BUT). After the tensile deformation the effective hydrogen diffusion coefficient became higher and it corresponded to the values of $1{,}30 \cdot 10^{-6}$ $cm^2 \cdot s^{-1}$ for 5 % tensile deformation and of $1{,}15 \cdot 10^{-6}$ $cm^2 \cdot s^{-1}$ for 10 % tensile deformation. This result confirms that 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 slightly 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 the studied states. This phenomenon is related to the presence of retained austenite in the steel and it can, at least partially, explain rather high susceptibility of the TRIP steels to hydrogen embrittlement.

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Note: The responsible translator for the English language is Boris Škandera, Czech Republic