HYDROGEN DIFFUSION AND HYDROGEN PROVOKED DEGRADATION IN THE TRIP 800 Mn-Si-Al STEEL

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Abstract

The presented paper deals with hydrogen diffusion and hydrogen provoked degradation in the TRIP 800 Mn-Si-Al steel with increased aluminum content. The steel was studied after standard heat treatment including two step annealing - an intercritical annealing and an annealing in the range of bainitic transformation. A part of specimens was submitted to a plastic deformation in tension (5 and 10 %) in order to modify both structure and mechanical properties. Microstructure of the steel consisted predominantly of ferrite, bainite and retained austenite, the amount of which decreased with increasing extent of the plastic deformation. Hydrogen diffusion was studied by electrochemical permeation method. Hydrogen diffusion coefficients were calculated using the "time lag" method. The lowest values of hydrogen diffusion coefficients were always observed for the first build-up transient, while the highest values were recorded for the second build-up transient due to the less intense hydrogen trapping. As to the impact of deformation, the highest hydrogen diffusion coefficients were observed after 5 % tensile deformation. Subsurface hydrogen concentration reached maximal value approx. 14 mass ppm. Hydrogen embrittlement of the steel was studied using tensile tests after previous electrolytic charging in diluted sulfuric acid solution. Hydrogen embrittlement manifested itself mainly by a drop of elongation at fracture. As to the fracture morphology, hydrogen embrittlement resulted in a change of fracture mode from transgranular ductile fracture to transgranular cleavage fracture with an appearance of "fish eyes" initiated on aluminum rich non-metallic inclusions.

Keywords: TRIP steel, electrochemical permeation method, hydrogen diffusion, hydrogen embrittlement

1. INTRODUCTION

The need to reduce weight and increasing demands for safety in automotive applications are driving the development of advanced high-strength steels. Low alloy steels with a microstructure consisting of different phases are aimed at producing steels of greater strength without significantly deteriorating their ductility. One of these materials, referred to as TRIP (Transformation Induced Plasticity) steels, exhibit a complex multiphase microstructure that consists predominantly of a ferritic matrix together with grains of carbide-free bainite, metastable retained austenite and eventually some martensite [1, 2]. The retained austenite grains transform into martensite during deformation and this will delay the onset of necking, leading to a higher ductility by means of the TRIP effect. TRIP steels were initially based on the C-Mn-Si chemical composition [1]. Due to the fact that silicon may cause serious difficulties during hot-dip galvanizing, this element is often partially or totally replaced by aluminum [3]. Another benefit from the presence of aluminum is that Al accelerates the bainite formation, which is very important in the continuous industrial production. Aluminum, on the other hand, increases martensite start (M_s) temperature and destabilizes retained austenite in this way. Appropriate amount of the retained austenite in the TRIP steels (10 - 15 %) is however essential for the achievement of optimal mechanical properties [4].

As strength levels of the TRIP steels increase, hydrogen embrittlement of these steels receives increased attention and an understanding of fundamental mechanisms involved is of interest. Hydrogen diffusivities and solubilities vary greatly between ferrite and austenite and need to be considered in multiphase microstructures such as TRIP steels. Specifically, the room temperature hydrogen diffusivity in ferrite is high, while the corresponding diffusivity in austenite is very low. As a consequence of the low solubility coupled with the high mobility in ferrite, hydrogen is expected to be distributed inhomogeneously in the TRIP steel microstructures and may reside at traps, either reversible or irreversible. All kinds of the TRIP steels seem to be susceptible to hydrogen embrittlement [5]. This problem has also its practical importance as there is a risk of hydrogen embrittlement during acid pickling, an operation always preceding hot-dip galvanizing. Depover at al. [6] 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 studied materials. The authors correlated that behaviour 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. [7] 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 the hydrogen diffusion characteristics, which was shown quite clearly by Kim et al. [8].

In the present work attention was paid to the hydrogen diffusion characteristics as well as to the hydrogen embrittlement susceptibility in the TRIP 800 Mn-Si-Al steel in which silicon was partially replaced by aluminum. The steel was studied in three different states: in the as-received state (after both hot and cold rolling and a subsequent heat treatment) and furthermore after 5 % and 10 % tensile deformation to change both mechanical properties and microstructure of the steel.

2. EXPERIMENTAL METHODS

The TRIP 800 Mn-Si-Al 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 TRIP Mn-Si-Al steel (wt. %)

C	**Mn**	**Si**	**Al**	S	P	Mo	Cu	Cr
0.21	1.57	1.05	0.54	0.005	0.013	0.01	0.07	0.16

Details concerning steel manufacturing and its heat treatment can be found in [9]. Steel structure was observed using light microscopy (LM) and scanning electron microscopy (SEM) [9]. Retained austenite (RA) content was determined by means of X-ray analysis using Co K_α source (λ = 0.17902 nm). Mechanical properties were determined using a standard tensile test and they are given in **Table 2** together with the retained austenite content.

Table 2 Mechanical properties and retained austenite content in the TRIP Mn-Si-Al steel

State	**Yield strength (MPa)**	**Tensile strength (MPa)**	**Elongation at fracture (%)**	**Retained austenite content (%)**
as-received	438	842	34.0	14.8 ± 2.0
5 % deformation	728	889	27.8	11.3 ± 2.0
10 % deformation	884	971	23.2	7.9 ± 2.0

Hydrogen diffusion characteristics were studied using electrochemical permeation method based on Devanathan-Stachurski cell. The conditions of experiment were the same as those described in [10]. Two build-up transients (BUT) were recorded during permeation experiments, 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 the end of the experiment the hydrogen charging was stopped and a decay transient (DT) was also recorded. An example of obtained hydrogen permeation curve is shown in **Figure 1.**

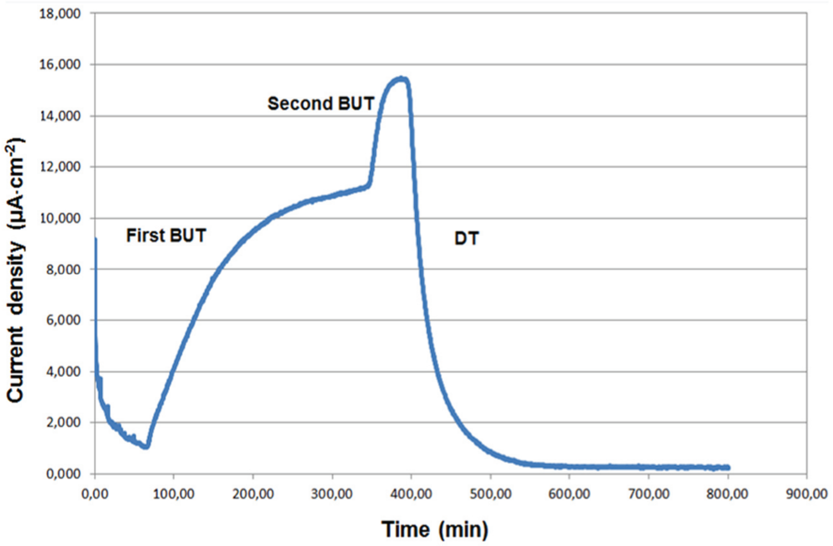


Figure 1 Example of hydrogen permeation curve for the Mn-Si-Al TRIP steel

Hydrogen embrittlement susceptibility of the TRIP Mn-Si-Al steel was studied by tensile test on previously hydrogen charged specimens. The hydrogen charging was performed in 0.05M H_2SO_4 solution with a specimen as a cathode at the current density of 1 mA·cm^{-2} for times going from 4 to 24 hours. Tensile testing was performed immediately after hydrogen charging at a strain rate 8.0 x 10^{-5} s^{-1}. The susceptibility to hydrogen embrittlement was expressed using so-called hydrogen embrittlement index *F*, which was equal to the ratio between the elongation at fracture of hydrogen charged specimen and the elongation at fracture of specimen non-charged. To complete this part of the investigation, fracture characteristics of both charged and non-charged specimens were obtained using SEM.

3. RESULTS AND DISCUSSION

3.1. Hydrogen diffusion characteristic of the TRIP Mn-Si-Al steel

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

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

where: *L* - membrane thickness (cm), t_L- time where the permeation currents reaches 63% of its steady-state value (s).

Sub-surface hydrogen concentration was calculated by the following equation:

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

where: i_∞ - steady-state current density (A·m^{-2}), *L* - membrane thickness (m), D_{eff} - effective diffusion coefficient (m^2·s^{-1}), *F* - Faraday´s constant (C·mol^{-1}).

The hydrogen diffusion coefficients are given in **Table 3** for all three studied states.

Table 3 Effective hydrogen diffusion coefficient D_{eff} for all studied states

State / part of a permeation curve	as-received D_{eff} ($cm^2 \cdot s^{-1}$)	5 % deformation D_{eff} ($cm^2 \cdot s^{-1}$)	10 % deformation D_{eff} ($cm^2 \cdot s^{-1}$)
first BUT	7.5×10^{-8}	9.0×10^{-8}	6.8×10^{-8}
second BUT	4.7×10^{-7}	5.9×10^{-7}	4.6×10^{-7}
DT	2.4×10^{-7}	2.5×10^{-7}	2.1×10^{-7}

It can be deduced from **Table 3** that the lowest and nearly the same 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. 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 coefficient was a little higher for the state after 5 % tensile deformation. This behaviour is in a good agreement with the results of Kim et al. [8]. For the decay transients the hydrogen diffusion coefficients were situated between the values obtained for the 1st and 2nd BUT. All measured values of hydrogen diffusion coefficient for the TRIP Mn-Si-Al steel were very low for a predominantly bcc steel and they were even lower in comparison with the values obtained for the TRIP Mn-Si-P studied earlier [10].

Hydrogen sub-surface concentrations were only calculated for the 1st BUT using Equation 2. The obtained results are presented in **Table 4.**

Table 4 Hydrogen sub-surface concentrations during the first BUT (mass ppm of H)

As-received	5 % tensile deformation	10 % tensile deformation
8.6	10.9	14.1

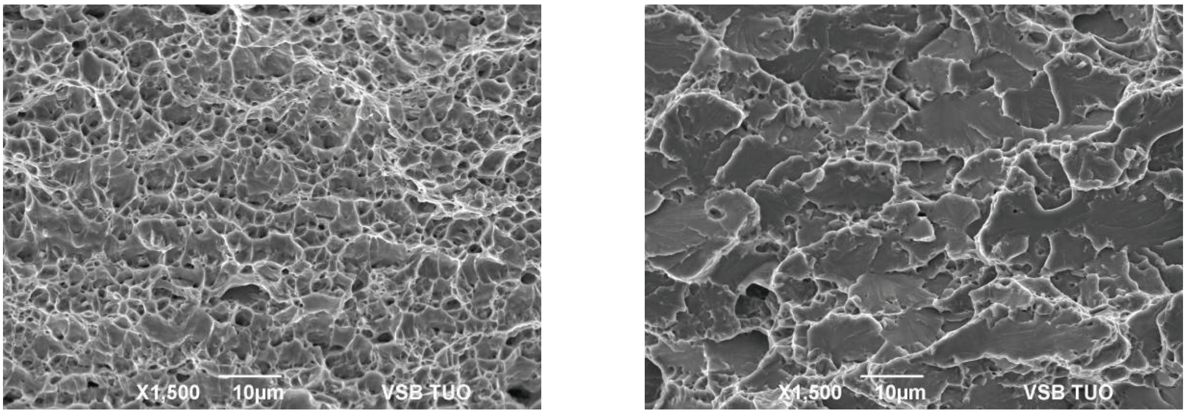
The calculated values are rather high for the steel having predominantly bcc lattice and it can be attributed to the presence of retained austenite in the structure. The observed increase of the hydrogen sub-surface concentration after tensile deformation can be related to the enhanced hydrogen absorption provoked by the higher dislocation density. On the other hand, the observed values are much lower in comparison with the values calculated for the TRIP Mn-Si-P steel [10]. This difference supports the fact that phosphorus can promote hydrogen absorption into the steel in a significant way.

3.2. Hydrogen embrittlement of the TRIP Mn-Si-Al steel

Hydrogen embrittlement of the TRIP Mn-Si-Al steel manifested itself mainly by a significant drop of elongation at fracture while the yield strength and ultimate tensile strength were only slightly changed. The lowest values of elongation at fracture were observed after 24 hour hydrogen charging. In **Table 5** values of hydrogen embrittlement index *F* are presented for the as-receive state and for times of hydrogen charging 4, 8 and 24 hours.

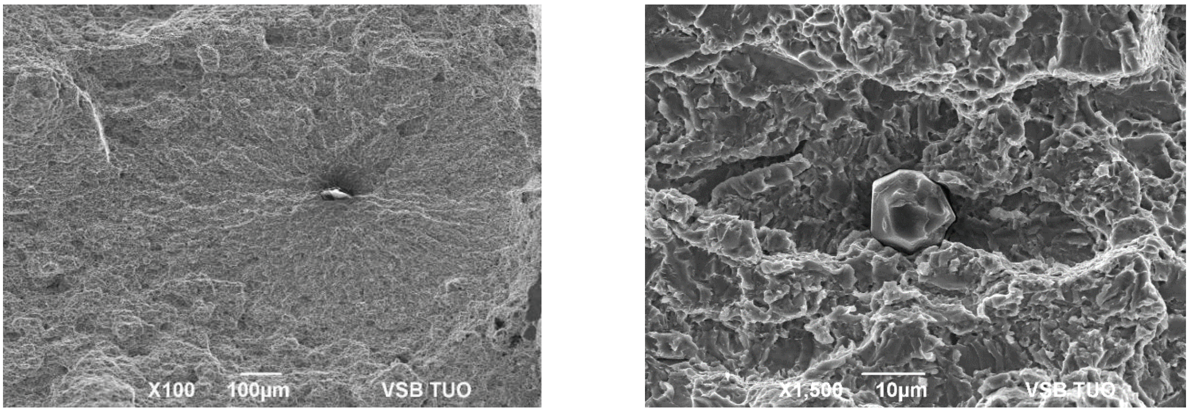
Table 5 Hydrogen embrittlement index *F* (%) calculated from the elongation at fracture

Charging time / Hydrogen embrittlement index *F* (%)		
4 hour hydrogen charging *F* (%)	**8 hour hydrogen charging *F* (%)**	**24 hour hydrogen charging *F* (%)**
74	68	82



a) Fracture surface of non-charged specimen

b) Fracture surface of hydrogen charged specimen



c) “Fish eye” on the fracture surface of hydrogen charged specimen

d) Al_2O_3 in the centre of the “fish eye”

Figure 2 Fractographic characteristics of the TRIP Mn-Si-Al steel

It is evident from the values of hydrogen embrittlement index *F* presented in **Table 5** that the susceptibility to hydrogen embrittlement was very high in the studied Mn-Si-Al TRIP steel. Even after rather short time of hydrogen charging, the hydrogen embrittlement index reached more than 70 %. It is in a good agreement with the results presented by Depover et al. [6] in another kind of the TRIP steel based on the Mn-Si composition. The fact that hydrogen embrittlement index *F* does not seem to depend on the charging time can be explained taking into account the specimen thickness and hydrogen diffusion coefficient. In fact, even for 4 hour hydrogen charging hydrogen can diffuse nearly through the whole specimen thickness.

Hydrogen embrittlement of the studied steel also resulted in a significant change of the fracture morphology. Transgranular ductile fracture was mainly observed on tensile specimens non-charged in hydrogen (**Figure 2a**), while transgranular cleavage fracture was dominant on hydrogen charged specimens (**Figure 2b**). Rather often, less or more circular areas of quasi-cleavage fracture were observed on fracture surfaces of hydrogen charged specimens (**Figure 2c**). These areas represent so-called “fish eyes”, defects provoked by hydrogen, initiating on non-metallic inclusions. The only inclusions found in the centre of the “fish eyes” were pure Al_2O_3 oxides in the studied case (**Figure 2d**).

4. CONCLUSIONS

The presented paper was devoted to evaluation of hydrogen diffusion characteristics and hydrogen embrittlement susceptibility in the Mn-Si-Al TRIP 800 steel.

The obtained results can be summarized as follows:

- Hydrogen diffusion coefficients of the TRIP Mn-Si-Al steel are very low even in comparison with some other TRIP steels and depend only slightly on the steel deformation;
- Hydrogen sub-surface concentrations are rather high, increase with the applied tensile deformation, but they are lower than in other TRIP steels studied earlier;
- The studied steel displays a high susceptibility to hydrogen embrittlement, which manifests itself mainly by a drop of elongation at fracture. Hydrogen changes the fracture morphology significantly, from transgranular ductile fracture to transgranular cleavage fracture, in which “fish eyes” initiated on Al_2O_3 -inclusions were observed.

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