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Recenzované vědecké články

Hydrogen Diffusion in the TRIP Steel 800 C-Mn-Si-Al

Difuze vodíku v ocelích TRIP 800 C-Mn-Si-Al

Ing. Taťána Kulová; **prof. Dr. Ing. Jaroslav Sojka**; **Ing. Petra Váňová, Ph.D.**

VŠB – Technical University of Ostrava, Faculty of Metallurgy and Materials Engineering, Department of Material Engineering, 17. listopadu 15/2172, 708 33 Ostrava-Poruba, Czech republic

The presented paper deals with hydrogen diffusion in the TRIP steel 800 Mn-Si-Al with an 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. Part of specimens was submitted to 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 the maximal value of approx. 14 mass ppm.

***Key words**: TRIP steel; electrochemical permeation method; hydrogen diffusion*

Předložený článek se zabývá difuzí vodíku v oceli TRIP 800 Mn-Si-Al se zvýšeným obsahem hliníku. Tepelné zpracování dané TRIP oceli se skládalo z pěti stupňů: rychlý ohřev, vlastní interkritické žíhání, rychlé ochlazování, izotermická výdrž na teplotě bainitické přeměny a ochlazování na pokojovou teplotu. Oceli byly studovány ve třech rozdílných stavech, a to ve stavu bez deformace, po 5 a 10% tahové deformaci. Toto rozlišení různých stavů vyplývá z toho, že oceli TRIP jsou při výrobě karoserie automobilů používány na konstrukční prvky, které jsou většinou finálně zpracovány tvářením za studena s nerovnoměrným rozložením deformace. Mikrostruktura oceli byla tvořena feritem, bainitem a zbytkovým austenitem, jehož obsah se snižuje se zvyšujícím se rozsahem plastické deformace. V některých místech se dal předpokládat výskyt martenzitu. Difuzní charakteristiky vodíku byly studovány pomocí metody elektrochemické permeace vodíku a difuzní koeficienty byly vypočítány pomocí tzv. metody „time lag". Difuzní koeficienty vodíku byly zaznamenány v 1. fázi vodíkování, což odráží intenzivní uchycování vodíku ve vratných a nevratných vodíkových pastech. V 2. fázi vodíkování byly vodíkové pasti částečně zaplněny, a proto byl zaznamenán vyšší difúzní koeficient vodíku. V poslední fázi, kdy bylo vodíkování ukončeno, byl difuzní koeficient vodíku opět nižší, což se dá vysvětlit tím, že při snížení obsahu difundujícího vodíku dochází k postupnému uvolňování vodíku z vratných pastí a ten je následně oxidován při výstupu na povrchu. Nejvyšší difuzní koeficient vodíku byl zaznamenán po 5% tahové deformaci. Podpovrchová koncentrace vodíku dosáhla hodnoty cca 14 ppm, což je hodnota poměrně vysoká a lze ji přičíst přítomnosti zbytkového austenitu ve struktuře.

***Klíčová slova**: ocel TRIP; metoda elektrochemické permeace; difuze*

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 offer a possibility of producing steels of higher strength without significantly deteriorating their ductility. One of these materials, referred to as TRIP steels (Transformation Induced Plasticity), exhibits a complex multiphase microstructure that consists predominantly of a ferritic matrix together with grains of carbide-free bainite, metastable retained austenite and possibly some martensite [1, 2]. The retained austenite grains transform into martensite during deformation and this delays 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]. The steel was studied in three different states: in the as-received state (after both hot and cold rolling and subsequent heat treatment) and furthermore after 5 % and 10 % tensile deformation in order to change both mechanical properties and microstructure of the steel.

1. Material and experimental procedure

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

Tab. 1 The chemical composition (wt. %)
Tab. 1 Chemické složení (hm. %)

TRIP 800	C	Mn	Si	Al	S
	0.21	1.57	1.05	0.54	0.005
P	**Mo**	**Cu**	**Cr**	**C**	**Mn**
0.013	0.01	0.07	0.16	0.21	1.57

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) (Fig. 1). Retained austenite (RA) content was determined by means of X-ray analysis using Co Kα source (λ = 0.17902 nm). Mechanical properties were determined using a standard tensile test and they are given in Tab. 2 together with the retained austenite content.

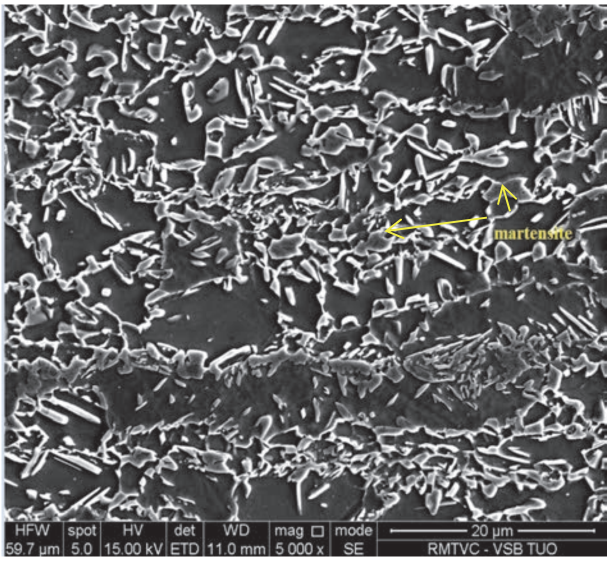

Fig. 1 Microstructure after deformation of 5 % (SEM)
Obr. 1 Mikrostruktura po 5% deformaci (SEM)

Permeation of hydrogen includes all events, which are associated with the permeation of hydrogen trough thin metal membrane. This method is the most common tool used to determine the diffusion coefficient of metallic materials. The electrochemical permeation technique was developed by Devanathan–Stachurski in 1962. Two-component cell is separated by a steel membrane – working electrode. Both sides of the working electrode were polished mechanically with the use of grinding paper up to 1200. After that, the exit side of the working electrode was palladium coated in order to prevent a hydrogen atom recombination during permeation experiments [3]. Hydrogen charging cell was filled with 0.05M H_2SO_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. The hydrogen permeation current was recorded using a VOLTALAB 40 potentiostat during experiments.

Tab. 2 Mechanical properties and retained austenite content in the TRIP steel Mn-Si-Al
Tab. 2 Mechanické vlastnosti a obsah zbytkového austenitu v oceli TRIP Mn-Si-Al

State	Yield strength	Tensile strength	Elongation at fracture	Retained austenite content
	(MPa)		(%)	
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

After an output current stabilization, the entry side of the specimen was polarized anodically at a current density of +35 mA·cm^{-2}. 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. An example of the obtained hydrogen permeation curve is shown in Fig. 2.

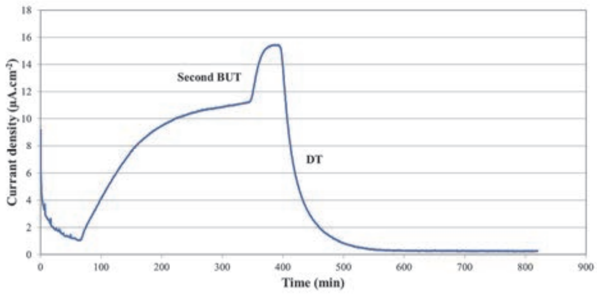

Fig. 2 Example of hydrogen permeation curve for the Mn-Si-Al TRIP steel
Obr. 2 Příklad permeační křivky oceli TRIP Mn-Si-Al

2. Results and discussion

Hydrogen diffusion characteristic of the TRIP steel Mn-Si-Al:

Hydrogen diffusion coefficients were calculated using the time-lag method expressed by the following equation:

$$D = \frac{L^2}{6 \cdot t_l}, \quad (1)$$

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 according to Eq. (2):

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

where: i_∞ – steady-state current density ($A \cdot m^{-2}$),

L – membrane thickness (m),

D – diffusion coefficient ($m^2 \cdot s^{-1}$),

F – Faraday´s constant ($C \cdot mol^{-1}$).

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

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 $D_{eff} \cdot t/L^2$.

Tab. 3 Effective hydrogen diffusion coefficient D_{eff} ($cm^2 \cdot s^{-1}$) for all studied states

Tab. 3 Hodnoty zdánlivého difúzního koeficientu vodíku D_{eff} ($cm^2 \cdot s^{-1}$) pro všechny studované stavy

State/part of a permeation curve	As-received	Deformation 5 %	Deformation 10 %
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 Tab. 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 they confirmed thus that the major part of traps was filled by hydrogen during the 1st BUT. In the case of the 2nd BUT the 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. [5]. For the decay transients the hydrogen diffusion coefficients were situated between the values obtained for the 1st and the 2nd BUT. All the measured values of hydrogen diffusion coefficient for the TRIP steel Mn-Si-Al were very low for a predominantly bcc steel and they were even lower in comparison with the values obtained for the TRIP steel Mn-Si-P studied earlier [6].

Hydrogen sub-surface concentrations were only calculated for the 1st BUT using Eq. (2). The obtained results are presented in Tab 4.

Tab. 4 Hydrogen sub-surface concentrations during the first BUT (ppm)

Tab. 4 Hodnoty podpovrchové koncentrace vodíku během 1. fáze vodíkování (ppm)

As-received	Tensile deformation 5 %	Tensile deformation 10 %
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 steel Mn-Si-P [6]. This difference supports the fact that phosphorus can significantly support hydrogen absorption into the steel.

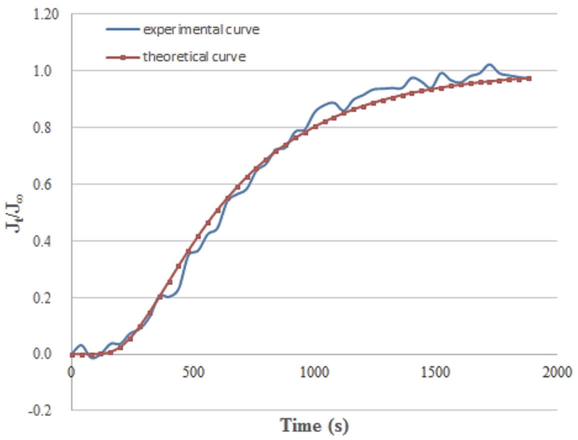

Fig. 3 Fitting the experimental data with the theoretical curve for the 2nd BUT after deformation of 5 %

Obr. 3 Srovnání experimentální a teoretické křivky ve 2. fázi vodíkování po 5% deformaci

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. The 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 a longer time in comparison with the theoretical curves confirming thus the important role of hydrogen trapping and de-trapping during the 1st BUT and during the DT [6].

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 steel Mn-Si-Al are very low even in comparison with some other TRIP steels and they depend only slightly on the steel deformation;
- Hydrogen sub-surface concentrations are rather high, they increase with the applied tensile deformation, but they are lower than in other TRIP steels studied earlier.

Acknowledgement

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Vývoj nové oceli

Stahlbau Nachrichten *4/2016*

Spolkové ministerstvo vzdělávání a výzkum podpoří projekt na vývoj nové oceli v Max-Planck institutu pro výzkum železa v Düsseldorfu částkou 1,5 milionu €. Těžko hledat něco společného v pojmech jako jsou větrné turbíny a železnice. Přesto mají něco společného: tzv. bíle naleptávané praskliny (White Etching Cracks), do značné míry zatím nevysvětlený škodlivý mechanismus, který se v nepředpověditelné době vyskytuje na mechanických kontaktních bodech a ročně způsobuje enormní škody. Proto jsou na celém světě železniční koleje v pravidelných intervalech obrušovány, aby se těmto škodám zabránilo. Ještě dramatičtější je situace u větrných elektráren, kde se podobné jevy vyskytují také a jejichž převodové mechanismy mohou být vyměňovány jen s velkými náklady. Tvorba těchto prasklin probíhá na tak malých délkových škálách, že nemohla být doposud zkoumána ani nejmodernějšími mikroskopy.

Slabé trhy a výpadky se u Evrazu 2016 postaraly o pokles výroby

Stahl Aktuell *20.01.2017*

Slabé trhy v odvětvích rour a kolejnic v Severní Americe jakož i menší výroba surové oceli u Evraz ZSMK na základě větších oprav by měly být hlavními důvody pro to, že výroba surové oceli u ruského výrobce oceli Evraz v roce 2016 v porovnání s předcházejícím rokem poklesla. Kromě toho hrála při tom roli také dekonzolidace Evraz Highveld Steel and Vanadium v dubnu 2015. V závěrečném čtvrtletí 2016 už ale nic neklesalo: výrobce oceli udržel výrobu surové oceli ve srovnání se třetím čtvrtletím stabilní s 3,4 mil. tun. Konzolidovaná výroba surové oceli byla ale podle údajů Evrazu v celém roce 2016 o 5,7 % nižší než v roce 2015, odbyt ocelářských výrobků klesl o 6,1 %.