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Hydrogen induced mechanical degradation in tungsten alloyed steels

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ABSTRACT

The present work considers the effect of hydrogen on the mechanical properties of generic Fe-C-W alloys. Thermal treatment aimed at a martensitic microstructure and two conditions are compared; i.e. an as-quenched state and a quenched and tempered state with lower dislocation density and with W based carbides formed during tempering. The hydrogen induced mechanical degradation is evaluated by in-situ tensile tests, while thermal desorption spectroscopy, hot/melt extraction and permeation experiments are performed to understand the observed hydrogen embrittlement degree. The hydrogen induced ductility loss increases with increasing carbon content due to the higher amount of hydrogen trapped by the denser martensitic lath boundaries. Furthermore, the quenched and tempered condition shows a lower susceptibility to hydrogen. This is correlated to the reduced hydrogen content when tempered due to a decreased dislocation density and the fact that the tempered induced W_2C particles did not trap hydrogen. Moreover, corresponding observations to this interpretation are perceived by permeation experiments since, on the one hand, the diffusion coefficient decreases with carbon content due to the increasing trapping ability of alloy A ➔ B ➔ C, and, on the other hand, the diffusivity increases when tempering is applied, which is also linked to the decrease in dislocation density and the disability of the carbides to hinder hydrogen diffusion by efficient trapping.

1. Introduction

Reducing the CO_2 emissions is one of the main universal challenges to diminish the global warming issues. In the automotive industry, decreasing the fossil fuel consumption by lowering the vehicle's weight has been considered a relevant strategy to meet the stringent CO_2 requirements. The use of high strength steels can both guarantee an increased safety together with weight reduction. However, these materials are considered to be prone to hydrogen induced mechanical degradation and therefore jeopardizing further steel development [1] [2]. Amongst others, dual phase (DP), transformation induced plasticity (TRIP) and high strength low alloyed (HSLA) steels are commonly used grades in the automotive industry and were already subject of multiple hydrogen related studies [3] [4] [5] [6] [7] [8] [9] [10] [11] [12] [13]. The impact of hydrogen on the mechanical properties was studied in [14], where the best resistance against hydrogen embrittlement was observed for the HSLA steel due to the presence of Ti and Nb carbonitrides.

However, these commercial high strength steels possess a multiphase microstructure, which complicates the interpretation of hydrogen related data. Therefore, single phase alloys or even single crystals were processed and have been under investigation as well [15] [16] [17] [18] [19] [20] [21] [22] [23]. Moreover, a relevant topic of study has been the role of precipitates on the hydrogen embrittlement. The presence of carbides is considered to be beneficial to strengthen the material and they are assumed to trap hydrogen efficiently. Inducing well-designed hydrogen trapping sites might be a relevant strategy to enhance the resistance to hydrogen induced failure as a limited amount of mobile hydrogen can already result into catastrophic consequences. Recently, Fe-C-X alloys were investigated in depth to analyze the trapping capacity of tempered induced Ti, V, Mo and Cr based carbides and their impact on the hydrogen induced mechanical degradation [24] [25] [26] [27]. All carbides were confirmed to show a beneficial impact on the hydrogen induced ductility loss and were able to trap a significant amount of hydrogen as determined by thermal desorption spectroscopy (TDS). The size and coherency were demonstrated to be crucial in terms of trapping ability; i.e. the small and coherent TiC [24] and V_4C_3 [25] precipitates of about 5–20 nm presented the best trapping efficiency, whereas coarser Mo_2C [26] and $Cr_{23}C_6$ [27] only trapped a limited amount of hydrogen. The role of W based carbides received only limited attention in literature so far and will be discussed in this work.

W is often used in tool steels since it is assumed to improve their wear resistance [28]. The A1 and A3 temperature increases and the martensitic start temperature decreases when tungsten is added [29]. At tempering temperatures between 500 °C and 700 °C, W_2C carbides

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are formed which are transformed into W_6C or $W_{23}C_6$ carbides when the temperature rises above 700 °C. The secondary hardening due to tempering is less pronounced compared to other carbide forming elements. This is attributed to the slow diffusion of tungsten, which delays the M_2C nucleation [30]. Kwon et al. [31] studied the secondary hardening in W alloyed steel and confirmed its limited secondary hardening capacity.

Little study has been done so far on the interaction of hydrogen with W based carbides. Recently, Zhoa et al. [32] investigated the effect of W on the hydrogen embrittlement in micro-alloyed steels. They examined four forging steels with different amounts of W. The amount of W had a large effect on the microstructure. The steel with 0 wt% W had a polygonal ferrite and pearlite structure, while the microstructure consisted out of bainite and acicular ferrite when 1 wt% W was added. These different phases display a different response to hydrogen [15] [33]. The diffusion of hydrogen in the pearlite structure is very high, since the boundaries of ferrite provide effective paths for hydrogen diffusion. The bainite structure, however, contains of a large amount of dislocations and the precipitated cementite between the ferrite acts as an obstacle for hydrogen transport. The effect of the microstructures on the diffusion of hydrogen was also observed by TDS. The hydrogen peaks were shifted to higher temperatures and the amount of hydrogen desorbed decreased when more W was added, indicating a decrease in diffusible hydrogen. Since no peaks with a high trapping activation energy were found, these authors linked the TDS peak with the amount of diffusible hydrogen, which they defined as trapping sites with lower activation energy. The addition of W induced a reduced TDS peak, which was considered proportional to the hydrogen concentration. Therefore, they stated that W addition decreased the amount of diffusible hydrogen under the same charging current density. However, this study showed that the difference in hydrogen/material interaction is not due to the formation of W carbides but due to the differences in obtained microstructure, caused by different amounts of W [32].

Malitckii [34] studied the effect of hydrogen on ODS-EUROFER and EUROFER97. The steels contained more than 1 wt% W and formed W carbides, while chromium carbides were also present. Tensile tests were performed on hydrogen charged samples. The different steels were electrochemically charged in an electrolyte consisting of 0.1 M NaOH with 20 mg/l $CS(NH_2)_2$ for 70 h. The time between charging and testing was 1 h. The tensile tests were carried out until rupture and afterwards, the fracture was observed by scanning and transmission electron microscopy. Hydrogen induced micro-cracks clearly initiated at the interface of the chromium and tungsten carbides, which were located at the grain boundaries. This can be an indication that hydrogen preferably diffuses to the tungsten carbides and is trapped there. However, several uncertainties remain and more investigation is clearly needed on the trapping capacity of W carbides in HSLA steels. Therefore, three different quenched and tempered martensitic structures will be considered and compared in this work to identify the role of these precipitates in a tempered martensitic matrix on the hydrogen/material interaction. Aspects such as the hydrogen embrittlement susceptibility, hydrogen trapping capacity and hydrogen diffusivity will be used to study this interaction.

2. Experimental Procedure

2.1. Material Characterization

Three generic Fe-C-W alloys with increasing carbon content were lab cast with a stoichiometric amount of the ternary alloying element, W. To avoid the formation of nitrides, Al was added to bind the present nitrogen. The carbon increase allows a reliable estimation of the impact of hydrogen on a variable strength level in different Fe-C-W alloys. The chemical compositions are given in Table 1.

Table 1
Chemical composition of the used materials in wt%.

Material/element	C	W	Other
Alloy A	0.096	2.670	150–200 ppm Al
Alloy B	0.186	6.130	10–15 ppm S
Alloy C	0.277	8.700	10–20 ppm P

The materials were processed in a Pfeiffer VSG100 incremental vacuum melting and casting unit under an argon gas atmosphere. Ingots with a size of 13 × 13 × 28 cm^3 were cast and sawn into 5 pieces with equal thickness. Slab reheating temperature before hot rolling was 1250 °C. Subsequently, hot rolling was done till 1.5 mm and an appropriate heat treatment was applied to obtain two main conditions. At first, an as quenched (as-Q) state and secondly, a quenched and tempered (Q&T) state, where free carbon is enabled to precipitate with W during tempering, is aimed for. Fig. 1 shows the temperature versus time profile of the applied heat treatment. The materials were austenitized at 1250 °C for 10 min to obtain a complete austenitic microstructure and to dissolve the carbides from earlier processing steps. These were then quenched in brine water (7 wt% NaCl) to obtain a fully martensitic structure. This condition will further be referred to as as-Q (Fig. 1 (a)). Next to the as-Q state, a second condition was prepared by tempering the quenched material at a certain temperature for one hour to induce W based carbides in the microstructure. The tempering stage was followed again by brine quenching (Fig. 1 (b)). Tempering was done at different temperatures to determine at which temperature the secondary hardening effect, due to the generation carbides, was most outspoken.

Vickers hardness measurements were performed to determine the as-Q hardness levels of the alloys and the tempering temperature at which secondary hardening was most effective, for which a weight of 2 kg and a pyramidal diamond tip was used. The microstructure was first examined by light optical microscopy (LOM), for which grinding, polishing and etching with 4% Nital for 10 s was done. Secondly, high resolution scanning electron microscopy (SEM) and transmission electron microscopy (TEM) allowed characterizing the carbides in terms of their size, size distribution and morphology. Carbon replicas and thin foils were prepared for this purpose. Carbon replication for SEM (Quanta FEG 450) analysis was made by sputtering carbon on top of a polished (1 μm) sample. Afterwards, carbides were extracted from the sample by putting it in a 4% Nital solution. An accelerating voltage of 20 kV was used together with a forward scatter detector (FSD) to characterize the carbides. Thin foil samples were prepared for STEM analysis (JEOL JEM-2200FS), at an accelerating voltage of 200 kV, by grinding and polishing the samples to a thickness below 100 μm. Subsequently, thin foils were electropolished with a TenuPol-5 electropolishing unit in a 10% perchloric acid and 90% acetic acid solution. The plate materials were further ground and tensile samples were machined with their tensile axis parallel to the rolling direction. Finally, the surfaces of the tensile samples were sandblasted to remove possible oxides remaining from processing. The specimen geometry is shown in Fig. 2.

2.2. Hydrogen Induced Mechanical Degradation

By comparing tensile tests performed in air with tests done on hydrogen saturated samples, the impact of hydrogen on the mechanical properties was determined. Hydrogen was introduced in the alloys by electrochemical pre-charging using a 1 g/l thiourea 0.5 M H_2SO_4 solution at a current density of 0.8 mA/cm^2 for 1 h, while in-situ charging continued during the tensile test. The conditions were chosen in such a way that a full saturation was guaranteed while no blisters or any internal damage was induced in the microstructure, as was confirmed by a similar procedure as described elsewhere [24]. The tensile tests were done at a cross-head displacement speed of 5 mm/min, which corresponds with a strain rate of $1.11 \times 10^{-3} s^{-1}$, similar to Zhao et al.