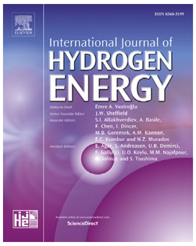
Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



The detrimental effect of hydrogen at dislocations on the hydrogen embrittlement susceptibility of Fe-C-X alloys: An experimental proof of the HELP mechanism

T. Depover[*], *K. Verbeken*

Department of Materials, Textiles and Chemical Engineering, Ghent University (UGent), Technologiepark 903, B-9052, Ghent, Belgium

A R T I C L E I N F O

Article history:
Received 27 October 2017
Received in revised form
14 December 2017
Accepted 16 December 2017
Available online xxx

Keywords:
Hydrogen embrittlement
Hydrogen trapping
Hydrogen dislocation mobility
HELP
Carbides

A B S T R A C T

The hydrogen trapping ability of 15 Fe-C-X alloys is compared in this work. Five types of carbides, i.e. Ti, Cr, Mo, W and V based carbides, and their effect on the hydrogen embrittlement susceptibility is considered while three carbon contents are prepared for each carbide former. Two conditions are compared for each alloy to evaluate the hydrogen/material interaction: an as quenched and quenched and tempered condition in which carbides are introduced. Next to the material characterization, also the interaction of hydrogen with the materials is completely elaborated. At first, in-situ tensile tests are done to determine the hydrogen induced ductility loss. To interpret the obtained degrees of hydrogen embrittlement, hot/melt extraction is done to determine the hydrogen content, whereas thermal desorption spectroscopy is performed to assess the hydrogen trapping capacity of the tempered induced precipitates and the different other potentially hydrogen trapping microstructural features. These measurements are done after hydrogen pre-charging till saturation. The tempered induced TiC and V_4C_3 are capable of trapping a significant amount of hydrogen, while the Mo_2C and $Cr_{23}C_6$ particles only trap a limited amount of hydrogen. The W_2C precipitates, however, are not able to trap hydrogen. The size and coherency of the carbides are considered to be the main factor determining their trapping ability. The degree of hydrogen embrittlement is correlated with the hydrogen present in the alloys. Three amounts of hydrogen were determined by the strength by which they were trapped by combining the different hydrogen characterization techniques, i.e. total, diffusible and mobile hydrogen. It was confirmed that hydrogen trapped by dislocations plays a determinant role. This further confirms the importance of an enhanced dislocation mobility in the presence of hydrogen, as described in the HELP mechanism.

Introduction

In the automotive industry, the harmful effect of hydrogen (H) on the mechanical properties of steels has been recently described to hinder further development of advanced high strength steels [1]. Though the detrimental effect of H was already discussed in 1875 by Johnson [2], no comprehensive understanding of the phenomenon behind the observed H

---

[*] *Corresponding author.*
E-mail address: Tom.Depover@ugent.be (T. Depover).

https://doi.org/10.1016/j.ijhydene.2017.12.109

Please cite this article in press as: Depover T, Verbeken K, The detrimental effect of hydrogen at dislocations on the hydrogen embrittlement susceptibility of Fe-C-X alloys: An experimental proof of the HELP mechanism, International Journal of Hydrogen Energy (2017), https://doi.org/10.1016/j.ijhydene.2017.12.109

induced ductility loss has been achieved up to now. Several mechanisms have been suggested to describe hydrogen embrittlement (HE), but no one has been fully accepted since indications linked to the different mechanisms have been observed experimentally. The three most cited mechanisms in non-hydride forming materials are the Hydrogen Enhanced DEcohesion (HEDE) [3], the Hydrogen Enhanced Localized Plasticity (HELP) [4] and Adsorption Induced Dislocation Emission (AIDE) theory [5,6]. HEDE considers a reduction in the cohesive bond strength between the metal atoms in the presence of H. This causes brittle crack propagation under tensile load. HELP proposes an increase in dislocation mobility in the presence of H, which results into highly localized plastic deformation and faster failure. This mechanism has attained substantial support [7–9], even though embrittlement together with enhanced plasticity seems to be contradictory. AIDE is comparable to HELP since AIDE also involves localized plasticity. However, AIDE also proposes that the localized plasticity occurs close to the surface at regions of stress concentrations, for instance at crack tips. The AIDE mechanism is based on dislocation emission from the surface due to H adsorption, inducing nanovoids in front of the crack tip due to stress localization.

Advanced high strength steels are considered to be very promising future materials for body in white components in the automotive industry since they combine a high strength level together with weight reduction. Consequently, both the safety can be guaranteed and more stringent CO_2 emission regulations can be met. However, steels with an increased strength level are assumed to be more susceptible to HE [10–13]. The interaction of these steels with H has been investigated in much detail during the last decade [14–19]. Moreover, we recently presented results on four industrial high strength steels, i.e. ferrite-bainite (FB), dual phase (DP), transformation induced plasticity (TRIP) and high strength low alloy steel (HSLA) [11,20–23]. The H induced ductility loss was specifically considered in Ref. [11] and a substantial degree of HE was detected, except for the HSLA steel, which was attributed to the presence of Ti- and Nb- carbo-nitrides, indicating their beneficial impact. The major drawback of these studies on industrial steels is their multiphase microstructure which complicates the interpretation of the H related phenomena. Therefore, materials with simplified microstructures allow a more straightforward interpretation.

The introduction of precipitates has been considered to be a relevant strategy for alloy development with improved resistance to hydrogen embrittlement [24,25], since they can both induce material strenghtening due to precipitation hardening and are often mentioned to act as an efficient deep H trapping site to remove the detrimental diffusible hydrogen from the microstructure [26–35]. Consequently, H is not present in the microstructure as highly diffusible H which is indeed assumed to be the most detrimental one. Wei et al. [36] showed that coherent and semi-coherent NbC, TiC and VC were capable of trapping H during electrochemical charging. Takahashi et al. [37] confirmed the presence of H at the interface of carbide and matrix by atom probe tomography as deuterium atoms were observed at the surfaces of nano-sized TiC. Di Stefano et al. [38] studied the H interaction with TiC in α-Fe by means of first-principles calculations based on density functional theory. They found a broad range of trapping sites for H going from different types of interfaces between the particle and matrix and carbon vacancies inside TiC. The latter was considered the most efficient one, although they were assumed to be difficult to activate at room temperature since the energy barrier for H entering the TiC is high. Wallaert et al. [39] showed that electrochemical cathodic charging resulted in H trapped near grain boundaries and at the interface of small NbC whereas gaseous charging at elevated temperature revealed deep trapping sites corresponding to H at incoherent NbC. Lee et al. [40] studied the effect of Mo/V based precipitates in tempered martensitic grades. V carbides were able to trap a significant amount of H due to the high chemical affinity of V for H. Vanadium carbides should be ideally present as VC although mainly V_4C_3 predominates. The empty carbon site can act as a physical trap for H [41]. The work of Spencer et al. [42] focused on the importance of Mo_2C with respect to HE resistance. Next to the impact of V carbides, Mo based precipitates also caused an additional beneficial effect enhancing the HE resistance. Thermal desorption spectroscopy (TDS) spectra of four steels containing NbC, TiC, VC and Mo_2C, respectively, revealed a descending order of trapping capacity, i.e. NbC > TiC >> VC > Mo_2C, indicating that Mo_2C was the least promising carbide [43]. Little has been reported on the trapping capacity of Cr and W based precipitates. Although TDS analysis showed the H trapping capacity of numerous carbides, research on their effect to the mechanical behavior in the presence of H is limited [42,44].

Trapping diffusible H using nano-sized carbides as trapping sites is generally accepted to be one of the main approaches to enhance the resistance against HE [11,36,42,45]. However, the complexity of the microstructure of industrial multiphase steel grades hinders the interpretation of experimental data. For that reason, well-designed Fe-C-X alloys were recently considered [46–50]. Ti, Cr, Mo, W and V (=X) were added as ternary carbide forming element and their impact on HE has been discussed focusing on one specific type of carbide forming element to fully comprehend the underlying mechanism taking place for each considered precipitate. However, a comparison between the different carbides is still missing. The present study aims to compare the tempered induced carbides to draw general conclusions in terms of their effect on the H induced mechanical degradation. An important asset in this context is that identical experimental procedures were used throughout the complete set of experiments. Materials processing as well as the study of the H/material interaction was done in an identical way for all alloys allowing a fair comparison of all different carbides.

Experimental procedure

Five different Fe-C-X grades with a stoichiometric amount of a ternary alloying element X were processed. Each grade was incrementally cast into three alloys with increasing carbon content (cf. Table 1). The carbon increase allows a reliable assessment of the effect of the carbides with varying strength level of the alloys and gives an opportunity to confirm their