

# COMPARISON OF THE ROLE OF FOUR DIFFERENT CARBIDES IN THE HYDROGEN INDUCED MECHANICAL DEGRADATION OF LAB CAST FE-C-X ALLOYS

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## ABSTRACT

The present work evaluates hydrogen trapping and hydrogen induced ductility loss of four lab cast Fe-C-X martensitic Q&T alloys. Ti, Mo, Cr and V are used as ternary alloying elements. The materials are compared in two conditions: as-Q and Q&T. Tensile tests are performed to evaluate H induced mechanical degradation. The hydrogen trapping capacity of the precipitates is investigated by TDS, while hot/melt extraction is done to determine the amount of hydrogen. A correlation between the degree of hydrogen induced mechanical degradation and the amount of hydrogen trapped by dislocations was observed.

## INTRODUCTION

In steel alloy development, the role of carbides has been a relevant topic [1]. They are also often cited to be beneficial as efficient H trapping sites. Although TDS studies showed the H trapping ability of several carbides [2-9], literature relating their impact on the mechanical properties in the presence of H is limited [10, 11]. However, steels with an increased strength level are considered to be prone to HE [12-14]. The interaction of these high strength steels with H has been studied thoroughly during the last decade [15, 16]. Recently, our group presented some results on four industrial multiphase high strength steels [17-22]. The mechanical properties were investigated as well [14] and a significant H induced ductility loss was observed, except for the HSLA (high strength low alloy) steel, which was attributed to the presence of Ti- and Nb- carbo-nitrides.

Recently, more and more emphasis is put on the addition of carbides as H trapping sites. Generally, trapping diffusible H using nano-sized carbides as H traps is one of the main strategies to enhance the resistance against HE [10, 14, 23]. However, the complex microstructure of multiphase steels hinders interpreting H related observations. Recently, we discussed specifically designed Fe-C-X alloys containing carbide forming elements, i.e. X = Ti, Cr, Mo and V [24-27]. However, each paper focused on one specific type of carbide forming element. The present study aims at making comparison between the different carbides.

## EXPERIMENTAL PROCEDURE

Four different steel grades with a stoichiometric amount of a ternary alloying element X (cf. Table 1) were processed. The Fe-C-X alloys were cast, hot rolled and subsequently austenitized at 1250°C for 10 minutes followed by a brine water quench. This first condition will be referred to as as-Q. Next, also a tempering treatment of 1h was applied to introduce carbides in the martensitic microstructure. Secondary hardening due to the precipitation of carbides was optimal at 600°C for the Fe-C-Ti, Fe-C-Mo and Fe-C-V alloys and at 550°C for the Fe-C-Cr material [24-27]. This second condition will be referred to as Q&T. The microstructure were studied by optical microscopy, SEM and TEM and the degree of H induced mechanical degradation, the H content and TDS measurements were determined as described in [24-27]. The %HE index was determined as:

$$\%HE = 100 \cdot \left(1 - \frac{\varepsilon_{ch}}{\varepsilon_{un}}\right)$$

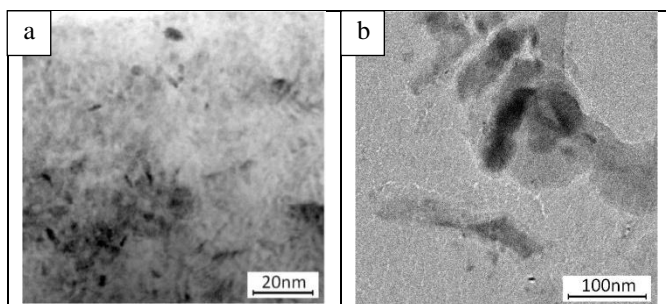
with  $\varepsilon_{ch}$  and  $\varepsilon_{un}$  being the elongation of the charged and uncharged sample, respectively. Hence, the %HE varies between 0 and 1, with 0 meaning that there is no ductility loss and the material is insensitive to HE. When an index of 1 is obtained, the ductility drop is 100% and HE is maximal.

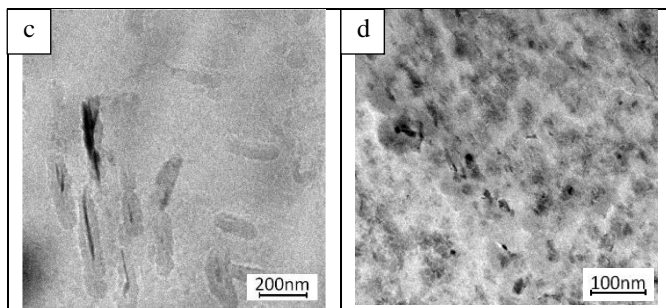
**Table 1: Chemical compositions of the Fe-C-X materials.**

Alloy Fe-C-X	wt.% C	wt.% X	Other elements
Fe-C-Ti	0.313	1.34	Al: 200-300 wt. ppm Other elements: traces
Fe-C-Cr	0.184	2.20	
Fe-C-Mo	0.177	2.99	
Fe-C-V	0.286	1.67	

## MATERIALS CHARACTERIZATION

Optical microscopy showed a clear martensitic and Q&T microstructure. TEM bright field images are presented in Fig. 1, and displayed small carbides with sizes less than 10 nm for the Ti- and V-alloy and coarser precipitates for the Mo- and Cr-alloy. More microstructural details can be found elsewhere [24-27].

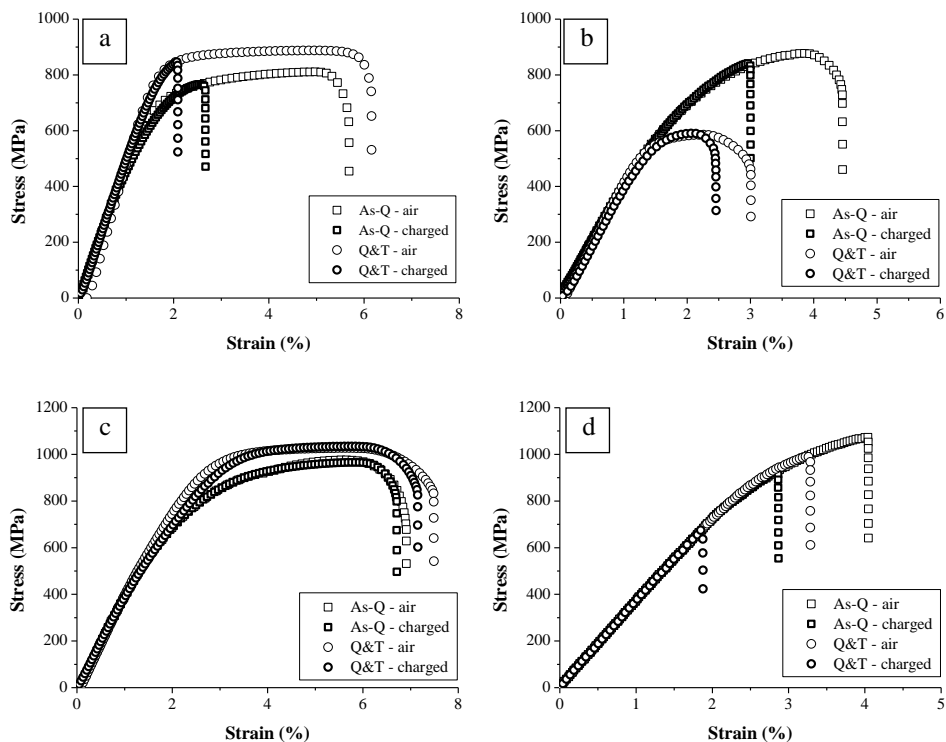




**Figure 1:** TEM bright field images of X-based carbides of the Fe-C-X alloys in Q&T condition, with X = Ti (a), Cr (b), Mo (c) and V (d).

## RESULTS AND DISCUSSION

The stress-strain curves for Ti-, Cr-, Mo- and V-alloy in the as-Q and Q&T condition are depicted in Fig. 2 and the degree of HE is given in Table 2. A significantly different HE susceptibility was observed for the four alloys.

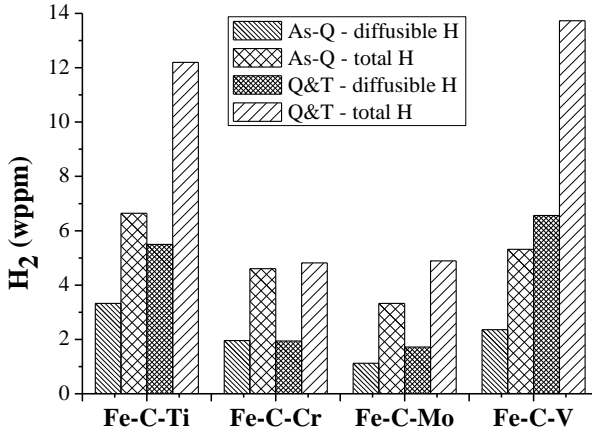


**Figure 2:** Stress-strain curves for (a) Fe-C-Ti, (b) Fe-C-Cr, (c) Fe-C-Mo and (d) Fe-C-V at a cross-head deformation speed of 5 mm/min of uncharged and H saturated samples.

**Table 2: The HE indices (% HE) of Fe-C-X alloys in the as-Q and Q&T conditions.**

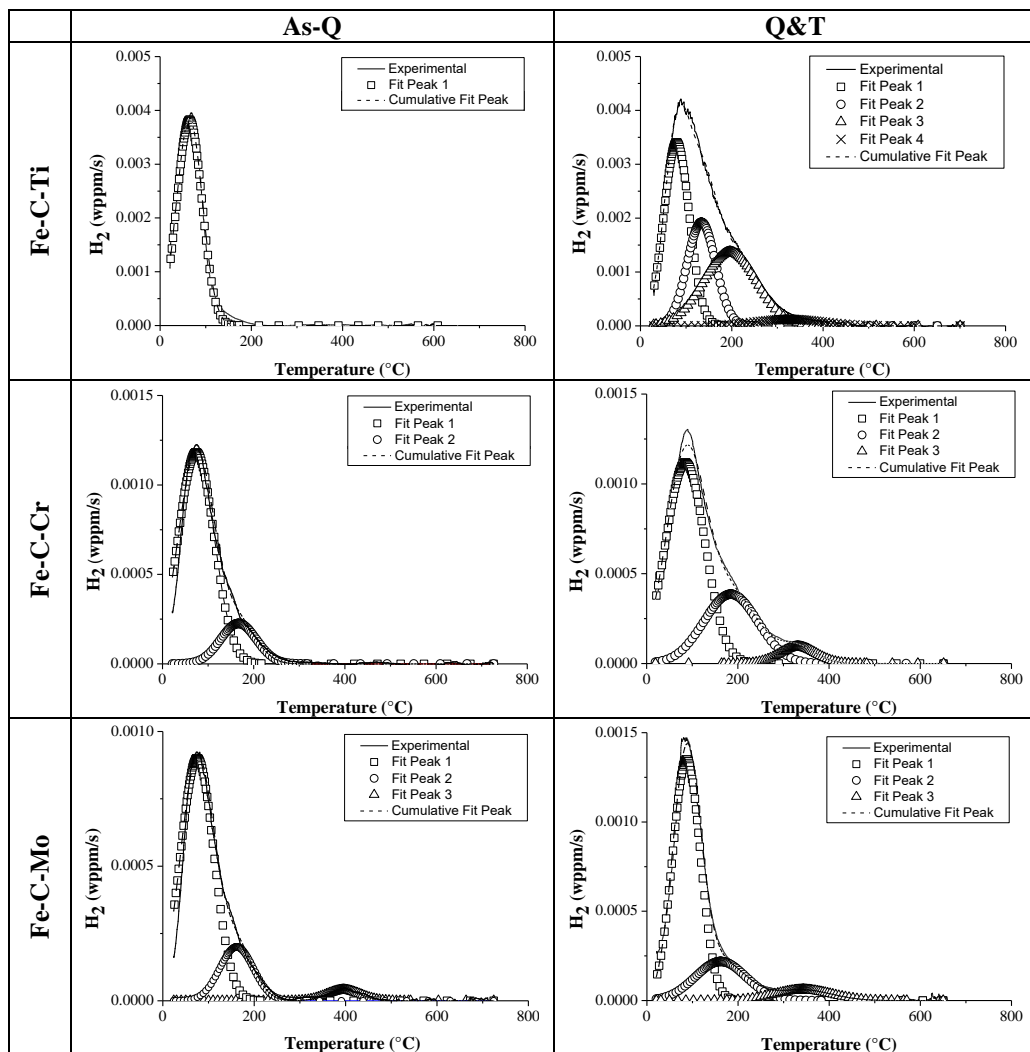
%HE	Fe-C-Ti		Fe-C-Cr		Fe-C-Mo		Fe-C-V	
	As-Q	Q&T	As-Q	Q&T	As-Q	Q&T	As-Q	Q&T
	53	66	33	18	3	5	29	43

To elaborate these results, hot (at 300°C) and melt (at 1600°C) extraction, which shows the diffusible and total H content of the H saturated samples, are given in Fig. 3. For the Fe-C-Ti and Fe-C-V materials, the diffusible and total H content nearly or more than doubled when the sample was tempered. Consequently, the microstructural changes that occurred during tempering, mainly the formation of a considerable amount of small Ti or V-carbides, provided an important increase in H trapping sites in the material (cf. TDS results). The Mo- and Cr-alloys showed a significantly lower H content, while the amount of diffusible H was the lowest for the Fe-C-Mo alloy. Moreover, the difference between as-Q and Q&T was also rather small, especially for Fe-C-Cr. Although tempering induced significant microstructural changes as well and therefore, also in the potential trapping sites, the H trapping capacity of both conditions appeared to be similar.

**Figure 3: Diffusible and total H content for saturated Ti-, Cr-, Mo- and V-alloys in the as-Q and Q&T condition.**

TDS was performed on all Fe-C-X alloys in both the as-Q and Q&T condition as summarized in Fig. 4. Basically, the first peak can be correlated to H trapped by lath boundaries, while the other peaks are linked to H trapped by the carbides. A more detailed interpretation of these data including  $E_a$  can be found elsewhere [24-27]. An overview of the H contents is given in Table 3. There is a clear difference between the amount of H as determined by hot extraction, i.e. diffusible H, and the total area under the TDS curve. Indeed, H was able leave the sample before the TDS measurement. This type of H will be defined as mobile H [24-27]. As demonstrated [19], traps such as dislocations indeed trap H, but loose it before the measurement started, as it took about 1h to reach a sufficiently low vacuum in the TDS chamber. During the tensile tests, however,

this mobile H is still present and relevant for the obtained results as discussed below.



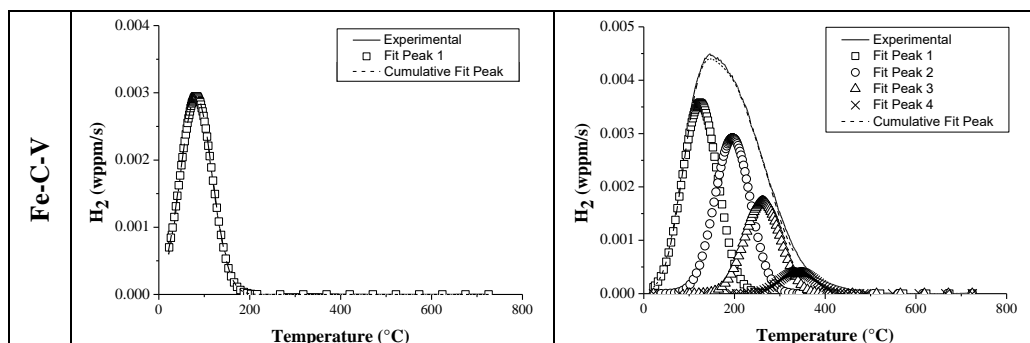


Figure 4: TDS curves of Fe-C-X alloys in the as-Q and Q&T condition (600°C/h).

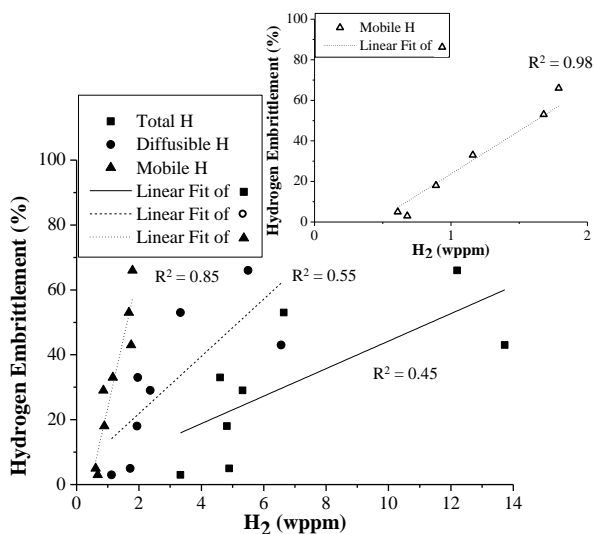
Table 3: The H contents of the Fe-C-X alloys in the as-Q and Q&T condition.

Hydrogen content (wppm)	Fe-C-Ti		Fe-C-Cr		Fe-C-Mo		Fe-C-V	
	As-Q	Q&T	As-Q	Q&T	As-Q	Q&T	As-Q	Q&T
diffusible hydrogen	3.33	5.50	1.96	1.94	1.12	1.72	2.36	6.56
hydrogen under TDS	1.65	3.90	0.80	1.10	0.50	1.17	1.50	5.28
mobile hydrogen	1.68	1.79	1.16	0.89	0.68	0.61	0.86	1.75

The HE degree is high (cf. Table 2) for the Fe-C-Ti alloys due to the high amount of H. Additionally, both Ti-alloys contained a similar and high amount of mobile H. Tempering even increased the HE to 66%. This could be attributed to the TiC precipitates formed during tempering, which not only increased the H trapping capacity as compared to the as-Q samples, but also introduced weakly trapped H at the elastic stress fields in the matrix surrounding the particle [6, 26]. The as-Q Cr-alloy embrittled more than the Q&T material although a similar amount of diffusible H was measured. However, due to the trapping ability of the carbides in the Q&T state, more mobile H was present in the as-Q material. Consequently, the Q&T alloy showed a lower HE [24]. The Fe-C-Mo alloys showed a much better resistance to HE, as almost no ductility loss is observed. First of all, the lower H content can account for this observation. Moreover, the amount of mobile H, was the lowest for this grade [25]. Finally, the Fe-C-V alloys showed rather low strain levels and the H charged specimen broke in the elastic region of the stress-strain curve. Tempering increased the sensitivity to HE. The higher amount of H, trapped by the V-carbides, can explain this observation. Since no or hardly any plastic deformation occurred for these alloys, the effect of mobile H, trapped at dislocations, is assumed to be minimal [27], as discussed below.

To confirm the hypothesis on the correlation between the HE degree and the amount of mobile H, the relation between the different types of H (i.e. total, diffusible and mobile) and HE is plotted together with a linear fitting (cf. Fig. 5). The correlation improves for total over diffusible to mobile H. Moreover, when the Fe-C-V materials are excluded, a  $R^2$  of 98% between the HE% and the amount of mobile H is obtained. This confirmed the crucial importance of the

amount of H trapped by dislocations and the enhancement of the dislocation mobility by the presence of H as proposed by the HELP mechanism.



**Figure 5: Degree of HE vs. the total, diffusible and mobile H content for Fe-C-X alloys. The Fe-C-V alloys were excluded from the data presented in the upper right corner, to illustrate very nicely the correlation between mobile H and HE for alloys where the sample broke past the macroscopic yield strength.**

## CONCLUSIONS

Four lab cast Fe-C-X materials (with X = Ti, Cr, Mo or V) were investigated in both as-Q and Q&T condition. The effect of the present carbides on the H trapping and HE was evaluated. The tempered induced carbides trapped a significant amount of H. The amount of mobile H, associated with H trapped at the dislocations, appeared to play a determinant role in the degree of HE. This was nicely illustrated by a correlation between the degree of HE and the amount of mobile H. The improved relation when the Fe-C-V materials were excluded from the correlation confirmed the importance of an enhanced dislocation mobility in the presence of H, i.e. the HELP mechanism.

## ACKNOWLEDGEMENTS

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