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Effect of Ti, Mo and Cr based precipitates on the hydrogen trapping and embrittlement of Fe–C–X Q&T alloys

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ABSTRACT

The present work evaluates hydrogen trapping and embrittlement (HE) for different laboratory cast Fe–C–X alloys with Ti, Mo and Cr (=X). Tempering generated X-based precipitates. The materials were examined under two conditions, as quenched and quenched and tempered. The hydrogen trapping capacity of the precipitates and matrix was investigated by thermal desorption spectroscopy (TDS), while hot and melt extraction, performed after cathodic charging, allowed to determine the diffusible and total hydrogen content, respectively. In-situ hydrogen pre-charged tensile specimens were tested to evaluate the hydrogen induced ductility loss. The different carbides exhibited a variable effect on the hydrogen embrittlement. The Fe–C–Ti material embrittled the most and tempering even increased its HE-susceptibility, whereas the opposite was observed for the Fe–C–Cr grade. Finally, the HE-resistance was best for the Fe–C–Mo alloys. Correlation between the mechanical behavior and the TDS and hot/melt extraction results was made as well.

Introduction

Hydrogen is frequently mentioned as an important energy carrier for future applications since it serves as an ecological alternative for the decreasing fossil fuel stocks [1]. Combustion only produces water from which it was initially derived. Therefore, it could avoid CO_2 emissions, which are claimed to have an important impact on global warming. However, the commercialization of hydrogen has proven to be a challenge in terms of transportation [2] and storage [3], including some material related issues and unpredictable failures [3]. Consequently, thorough investigation on the material-hydrogen interactions is of great importance and interest.

The phenomenon of hydrogen embrittlement (HE) is also of great interest for the automotive industry where focus is put on steels with a high strength level. Moreover, lowering the weight of vehicles is essential to reduce the polluting emissions. Due to their good combination of high strength and low weight, multiphase high-strength steels are good candidates to meet these desires, but unfortunately these materials suffer from some HE-related issues [4–6]. Nevertheless, the complex microstructure of these multiphase high strength steels is a complicating issue when evaluating their interaction with

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hydrogen. This hydrogen/material interaction has been investigated previously by the present authors for industrial multiphase high strength steels with a complex combination of different microstructural constituents [7–11].

Pérez Escobar et al. [9,12] presented a correlation between the response of blister formation on electrochemical hydrogen charging and the way how hydrogen is present in the material. Unfortunately, thermal desorption spectroscopy (TDS) results revealed similar activation energies for the different microstructural constituents in the laboratory alloys showing the difficulty of correlating TDS spectra to a certain microstructural feature. Another work [4] focused on the hydrogen induced mechanical degradation of industrial steels, which was higher when the tensile test cross-head deformation speed was decreased due to the importance of the amount of diffusible hydrogen. This hydrogen diffusion/material interaction has also been studied in Refs. [11], where emphasis was put on the impact of mobile hydrogen on the hydrogen induced ductility loss and its reversible character since ductility was recovered after discharging for one week. However, the multiphase microstructure of these industrial steels is a complicating issue. Even in the detailed study on the transformation induced plasticity (TRIP) steel [7], where several material characterization techniques were combined with TDS, no conclusive interpretation of all peaks to a certain microstructural constituent was possible.

It is widely accepted that the susceptibility to hydrogen embrittlement is correlated with the microstructural characteristics of the material. Consequently, focus is put on simplified laboratory cast materials in this study, which allow to study some of these characteristics in more detail.

Carbides are often mentioned to have a positive effect on the HE susceptibility [4,11]. In one of the first studies on hydrogen trapping by TiC, Pressouyre and Bernstein [13] determined the detrapping activation energy (E_a) and concluded that coherent TiC were less effective in terms of hydrogen trapping compared to incoherent carbides, whereas the E_a increased with carbide size. Later on, Lee and Lee [14] presented a model for hydrogen trapping at the particle-matrix interface and demonstrated that incoherent TiC have a larger E_a than semi-coherent traps.

Wei et al. [15] determined the E_a for hydrogen from the incoherent TiC particles in a 0.05C–0.22Ti–2.0Ni steel to be 85.7 kJ/mol, while in another steel (0.42C–0.30Ti) with larger incoherent TiC the E_a was about 116 kJ/mol, whereas the coherent precipitates showed an E_a between 46 and 59 kJ/mol. Consequently, it could be assumed that the degree of coherence between matrix and precipitate plays a crucial role. Furthermore, Wei and Tsuzaki [16] also found that the amount of trapped hydrogen at (semi-) coherent TiC precipitates could be correlated with the amount of interfacial area, suggesting that hydrogen is trapped at the TiC/matrix interface. This was later confirmed by the work of Takahashi et al. [17].

Escobar et al. [18] investigated the interaction between TiC and hydrogen in a laboratory cast material which was charged cathodically and gaseously at high temperature. They revealed by means of TDS a high temperature peak which was attributed to irreversible trapping of hydrogen by TiC. Cathodic charging was not sufficient for hydrogen to get trapped by the incoherent TiC precipitates. A heat treatment at high temperature was needed as also confirmed by Wei and Tsuzaki [16]. Gaseous and electrochemical hydrogen charging activated a different kind of trapping site. The interaction between hydrogen and Ti and Nb-based second phase particles has been evaluated to some extent as well by our group [19–21].

Less information is available in literature on the interaction between Cr and Mo-based precipitates with hydrogen and on their effect of the HE susceptibility. Spencer et al. [22] found a lower embrittlement index when a higher concentration of Mo was present, indicating that Mo carbides might have a positive effect on the HE susceptibility. On the contrary, needle shaped Mo_2C precipitates are considered to be less effective compared to TiC in terms of trapping capacity [23]. Furthermore, Yamasaki and Bhadeshia [24] investigated the precipitation of Mo_2C in ternary Fe–C–Mo alloys with the aim of introducing hydrogen trapping sites. Modeling of the precipitation resulted in a good insight in the carbide formation, although no experimental evaluation of the hydrogen-carbide interaction was incorporated in the study.

Marchetti et al. [25] studied the influence of hydrogen on the mechanical properties in a tempered 9% Cr–1% Mo steel and an increasing ductility loss was observed with higher applied current density. However, they did not focus on the particular influence of the Cr alloying on the embrittlement behavior.

Though it is generally assumed that inhibiting diffusible hydrogen by introducing nano-carbides as hydrogen trap is a valid approach to reduce the HE susceptibility, a fundamental understanding is lacking. This work focusses on laboratory cast Fe–C–X martensitic alloys and aims to evaluate the hydrogen trapping capacity and ductility loss in an as quenched (as-Q) and a quenched and tempered (Q&T) grade in which Ti, Mo or Cr carbides are introduced.

Materials and methods

Material processing

Three different steel grades with a stoichiometric amount of ternary alloying element X (Table 1) were cast and processed. Besides carbon and the alloying element, also some Al was added to bind with N, and as such avoiding nitride formation.

The Fe–C–X alloys were produced in a Pfeiffer VSG100 vacuum melting and casting unit, operating under an argon gas protective atmosphere. The materials were further hot rolled till 1.5 mm and austenitized at 1250 °C for 10 min followed by a brine water quenching. Subsequently, a tempering treatment of 1 h was applied to introduce carbides in the martensitic microstructure. Since the size, coherency and

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
Fe–C–Mo	0.177	2.99	Other elements traces
Fe–C–Cr	0.184	2.20	