Changing the interfacial composition of carbide precipitates in metals and its effect on hydrogen trapping

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ABSTRACT

Hydrogen trapping at metal/carbide interfaces is changed with changing interfacial composition. This has been exemplified for the iron/vanadium carbide (VC) interface. It will be assumed that the carbide interface is a (100)-plane having a composition between the limiting cases of either 50% V and 50% C for excess carbon in iron or 50% V and 50% carbon-vacancies for excess vanadium in iron. The latter will provide strong traps for hydrogen. For validating the simple model a modified interpretation of published atom probe and thermal desorption data became necessary as discussed in the present work.

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In the framework of hydrogen embrittlement interfaces between carbide precipitates and iron play an important role. Hydrogen embrittlement of steels is observed by an accelerated crack growth during fatigue test, a reduced strain to failure during dynamic strain tests or a related increase of fracture surface [1–3]. These phenomena require a certain supply of hydrogen to the advancing crack tip, which may be quantified as the change of hydrogen concentration by Fick's Second Law [4,5].

In steels carbides are strong traps and the binding energy of hydrogen to these traps has been determined experimentally and by first principle calculations for a variety of carbides [6–9]. Among these vanadium carbide (VC or V_4C_3) has been characterized recently in an outstanding study [10] regarding sample preparation. The austenite/ferrite transformation and concomitant dislocation generation was avoided, which otherwise would have overshadowed trapping by the carbide precipitates. The work is also outstanding by using all relevant state of the art analytical tools as atom probe tomography (APT), thermal desorption spectroscopy (TDS) and high resolution transmission electron microscopy (HRTEM). It was clearly demonstrated by APT that hydrogen segregates to the iron/carbide-interface with a (100) orientation of the VC in the peak aged and over-aged samples (aging with respect to mechanical strength at 610 °C). It could be ruled out the hydrogen is entering the carbide as claimed in Ref. [11]. Besides this, the nature of the interface traps was identified as carbon vacancies by APT showing an excess of vanadium and by ruling out misfit dislocations by HRTEM, i.e. the carbides were precipitates with a coherent interface.

Thus hydrogen can be trapped in octahedral sites composed of five V-atoms and one Fe-atom. APT samples were charged with deuterium instead of hydrogen to avoid strong background contributions. For the sake of simplicity it will be avoided to distinguish between the two isotopes in the following. Another interesting insight into the trap behavior of carbides was provided in the same study by revealing that carbides in under-aged samples do not trap much hydrogen as measured by TDS and APT and interpreted by the fact that no excess vanadium was measured by APT. The H-binding energy of about 60 kJ/mol-H was reported in Ref. [10] without presenting the corresponding Kissinger Plot.

The chemistry of the interface of precipitates plays an important role, if it comes to hydrogen trapping. This is proven for oxide precipitates in palladium and silver [12–14]. In MgO vacancies at the interface are filled with oxygen leading to a composition of Mg_1O_{1+x} with $x \to 0$ for increasing volume of the precipitates [14]. It will be shown in the present study that this may be true for VC as well, i.e. only vacancies at the interface due to missing carbon lead to non-stoichiometric $V_{1+x}C_1$. This is different to the interpretation in Ref. [10], where V_4C_3 ($x = 1/3$) is assumed to form with vacancies being at both the interface and the bulk of VC. The interpretation in Ref. [10] appeared to be conclusive in the light of H-coverage being much <50% at the interface and the large binding energy of about 60 kJ/mol-H. The large binding energy is ruling out hydrogen losses during careful handling of APT-samples. However, a more sophisticated analysis of the TDS data of Ref. [10] is conducted in this work yielding a much lower binding energy and, therefore, allowing both no saturation of interfaces during hydrogen charging and/or losses during sample handling and mounting. Thus it can be shown that the total number of available traps is much larger, which

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finally justifies the conclusion that all hydrogen traps are carbon vacancies at the VC/iron-interface.

Changes of the interfacial composition for oxides and carbides are presented by a schematic presentation in Fig. 1. The two limiting cases for the (111) interface of oxides of either having 50% or 100% oxygen is depicted in Fig. 1a and b. Fig. 1 also shows the composition of the (100) VC/Fe-interface with its extreme cases of 50% carbon and 0% carbon. Whether the vacancies shown in Fig. 1 are filled with or approached by matrix atoms (Fe or Ag) has not been resolved yet. As shown in Refs. [12–14] the oxygen composition of the MgO-interfaces can be changed by annealing in oxygen (Fig. 1b) or in vacuum (Fig. 1a) leading to a change of hydrogen trapping.

The carbon composition of the VC is changed during the precipitation process itself. For short annealing (short aging times) the carbon activity near the interface is high, because the slowly moving vanadium is consumed by the precipitation without sufficient supply from the nearby iron matrix [10]. Then the interface composition resembles the one depicted in Fig. 1c. If the carbon in the Fe-matrix is consumed at higher annealing times, the higher initial concentration of vanadium in the Fe-matrix as realized in the steels of Ref. [10] finally leads to a higher vanadium activity near the interface and a composition as shown in Fig. 1d is attained. In under aged samples the carbides are formed as platelets with the composition VC. The carbon case as described in Ref. [10] and its modified interpretation are presented by the schematic presentations in Fig. 1c and d. They will be discussed in the following.

With a lattice constant of 0.415 nm for VC [16] the density of carbon vacancies on the (100) plane is 11.6 vacancies/nm^2 or $1.16 \cdot 10^{19}$ m^{-2}. According to Fig. 1d this should correspond to the interface coverage of hydrogen. However, the APT measurements yielded 0.6 ± 0.1 H/nm^2 only [10]. The much smaller experimental value may be interpreted in three ways.

1. The proposed model with all the carbon vacancies being at the interface is wrong and vacancies are also present in the carbide bulk, although not being occupied by hydrogen.

2. Part of the hydrogen may be lost during sample preparation or during the analysis at 60 K [17,18]. It has been shown in a different APT-study [18] that the freshly formed surfaces during field evaporation act as sinks for deuterium withdrawing it from the bulk and interfaces. Temperatures as low as 30 K [18] have to be reached to stop deuterium transport to the surface.

3. The binding energy is not sufficient to saturate the traps at the interface during hydrogen loading of the samples at 300 °C and 2 atm of hydrogen pressure.

It will be shown in the following by a refined evaluation of the TDS-data in Ref. [10] that the last two interpretations are valid and the assumption of 50% vacancies at the VC/Fe-interfaces is not contradicting experimental findings.

Hydrogen charging of the steel samples and subsequent TDS-analysis yields two types of peaks for under-aged and over-aged samples [10]. These are a low temperature peak for under-aged samples and a high temperature peak for peak- and over-aged samples. Following the conclusive interpretation in Ref. [10], the low temperature peaks stem from either dislocations or carbides formed in under-aged samples. These carbides precipitate as platelets and APT reveals the composition being that of VC. With increasing aging time the carbon in the lattice is finally consumed and the composition of the platelets corresponds then to V_4C_3 according to APT. This is consistent with maintaining the sodium chloride structure of VC and incorporating vacancies on the carbon-lattice being either in the bulk and/or the interface of the carbides. The same scenario is assumed in the present study with the exception that the carbon vacancies are not in the bulk but at the interface only (cf. Fig. 1). As shown later this scenario leads automatically to the composition V_4C_3 for the given thickness of the carbide platelets. The interface vacancies now appearing in the peak- and over-aged samples trap hydrogen with a binding energy being larger than the one for the under-aged samples and, therefore, the TDS peak appears at a higher temperature.

The evaluation takes advantage of equations of a recent study of TDS [19] exemplified for hydrogen in steel. In this study [19] the Kissinger Equation [20] was generalized for diffusion as the rate limiting step through a slab shaped sample. The generalized Kissinger Equation for cylindrical samples becomes

$$\ln\left[\frac{\theta}{T_m^2}\right] = \frac{E_t - Q}{RT_m} + \ln\left(\frac{2D_{fo}R\pi^2 c_o}{r^2 c_{to}(Q - E_t)}\right), \tag{1}$$
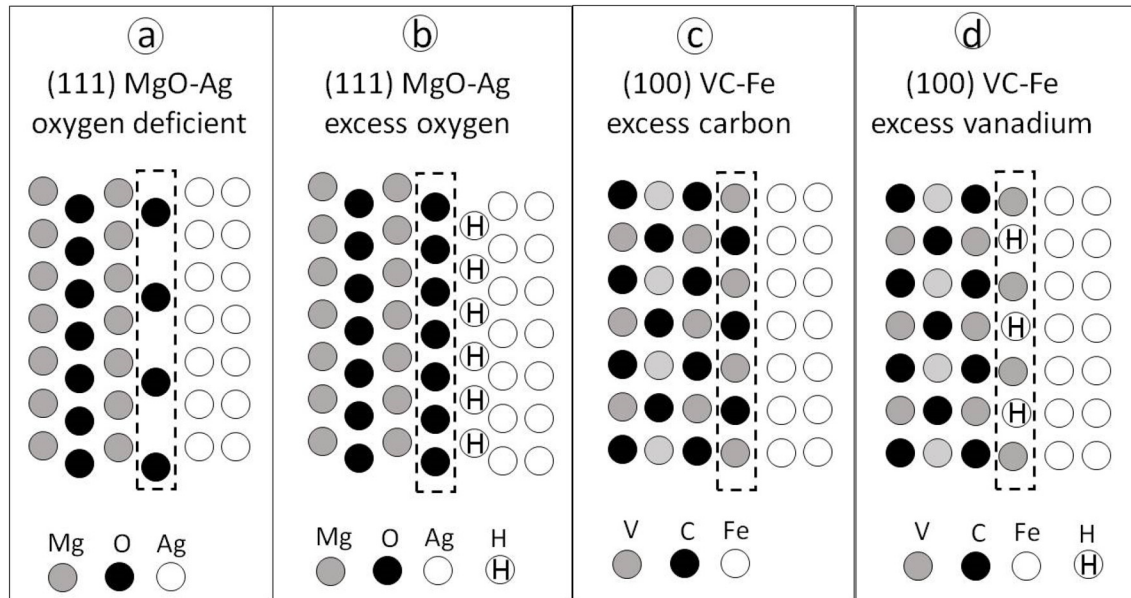
Fig. 1. The interface as surrounded by the dashed lines is defined as the atomic layer between the phases. The MgO/Ag-case is presented in a) and b) on the left hand side and the VC/Fe-case in c) and d) on the right hand side. The interface composition depends on the thermodynamic activity of the components in the metal or their concentrations respectively (corresponding small fraction of Mg and O-atoms in Ag or C- and V-atoms in Fe are not shown). As explained in the text and Refs. [12–15] strong trapping of hydrogen occurs, if the interface is 100% oxygen in the case of MgO (case b) or 0% carbon in the case of VC (case d).